ABSORPTION by DIFFERENT SOIL TYPES.

THE RELATIVE PROPORTIONS of EXCHANGEABLE BASES in some SCOTTISH SOILS.

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C O N T E N T S.

I N T R O D U C T I O N.

The soil possesses the very important property of retaining certain plant nutrients added to it. Whatever the mechanism of the action may be, this absorptive power of the soil enables it to maintain, in spite of leaching by rain, a store of material available for the plant, and, as will be pointed out later, has a most important bearing upon the physical and biological as well as the chemical properties of the soil. It was natural therefore that a problem of such practical and theoretical interest should claim the attention of agricultural chemists at an early date, and an enormous amount of work has been done on the subject.

From time to time different workers* have collected the available data and reviewed the subject, and therefore no attempt will be made to submit a complete account of the many investigations that have been carried out. It has been considered advisable however to deal briefly with the chief advances in order to show how present conceptions have arisen through the acceptance or rejection of the different views that have been expressed.

The subject may be divided roughly into three periods /

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*See references, 3,4,74,103,79,33,27, and 47.

periods. There was the awakening of interest in the subject with the quantitative measurements of Thomson and Way about 1850, the subsequent amassing of a large amount of data and the attempts to explain the various phenomena on insufficient chemical knowledge. There was a period of renewed interest dating from about 1880 with the attempt by van Bemmelen to apply the discoveries in the field of colloid chemistry to the behaviour of the soil. Then there has been the attack upon fundamental soil properties embracing soil formation and classification and the realisation that the soil is dynamic and a system so heterogeneous as to make it futile to regard it as a simple chemical compound or even a simple mixture. Thelast decade has seen a radical change in ideas and it would appear that this very important agricultural question is now being investigated in a thoroughly logical manner and without many of the limitations necessarily imposed upon it previously.

HISTORICAL REVIEW.

EARLY WORK.-

There is evidence that even in earliest times sand was employed to purify sea water, and by the beginning of the 19th century a number of investigators had observed that liquid manure could be clarified by percolation through fresh clay or loam, but Thomson[94] seems to have been the first to demonstrate the absorption of definite chemical substances accompanied by cation exchange. It is to Way[99,100] however that we are indebted for discoveries of such significance as to place the problem on a strictly scientific basis. The chemical knowledge of his time was such as to make the faculty of soils of separating ammonia appear extraordinary to him "inasmuch as there is no ordinary form of combination by which we could conceive ammonia to become combined in a state of insolubility in soil". He carried out percolation experiments with different soils, quantitatively with ammonium and potassium salts and qualitatively with magnesium, calcium and sodium salts and found that the absorption was confined to the + ve part of a neutral salt with an exchange of bases, and that the content of the - ve part remained unchanged. Furthermore he showed that the absorption was very rapid, was not proportional to the quantity of soil taken, was not affected much by temperature and was reduced by igniting /

igniting the soil. By means of a series of experiments he came to the conclusion that this power of the soil was not due to organic matter, sand or calcium carbonate and must be attributed to compounds of silica or clay, and he confirmed that by preparing artificial double silicates which possessed all the qualities of the clay itself. Way considered most carefully the explanations advanced previously by Liebig, who ascribed the absorption of ammonia to condensation of the gas by the aluminous and ferruginous compounds of the soil, and by Matteuci who suggested capillarity and selective adsorption, but he could not reconcile those ideas with the results he obtained with neutral salts and abandoned them in favour of a simple chemical explanation involving ordinary double decomposition with interchange of bases. His work reveals to an astonishing degree a remarkable knowledge of the principal features of the question and his practical recommendations at the conclusion of his second paper appear to be quite modern. He points out that intensive cultivation will allow the soil to fix the maximum amount of ammonia which in turn will release other bases in sufficient quantity for plant needs.

During the next twenty or thirty years numerous workers, particularly in Germany, investigated the empirical /

empirical side of the problem, confirming and modifying Way's results without discovering anything definitely new regarding this absorbing property beyond the fact that it was possessed by every soil. For example Henneberg and Stohmann (46) treated a soil with varying concentrations of ammonium salts and found that the absorption increased with the concentration but not proportionally, whilst Peters (75,76) working with solutions of potassium salts in different concentration and amount, showed that the absorption was never complete. Meantime Boedeker (8) made what was probably the first attempt to correlate the absorption with the concentrations of solutions in a mathematical treatment of the results of Henneberg and Stohmann. Salomon (87) measured the absorption of calcium from different concentrations by various soils, obtaining a series of most interesting results relating to the saturation of soils rich in humus, and about the same time work was done by Rautenberg (82) and Knop (60) with a view to discovering what constituent of the soil was the active agent in the absorption. Whilst the former arrived at the same conclusions as Way, Knop believed that the double silicates were responsible to a considerable extent at least. Little advance however was made in the knowledge of the character of absorption and the facts could not be reconciled /

reconciled with the chemical laws of the period. The Guldberg and Waage law of mass action was not formulated until 1867 and the data collected were so involved that it was not immediately realised that absorption is a reaction which is incomplete but proceeds to a definite equilibrium depending upon the concentration of the solution employed. The facts that sodium could set free calcium and on other occasions calcium could set free sodium, and that ammonium chloride could displace calcium from an insoluble silicate (although the ammonium silicate was soluble in water) were apparent inconsistencies which Liebig (62) at once criticised on chemical grounds. They were so contrary to his ideas on chemical reaction that he ascribed absorption to a physical surface attraction.

Knop (60) devised a method of determining what he called the "Absorptions-Koefficient" of a soil, by estimating the nitrogen taken up from 200 c.c. ·5 per cent. solution of ammonium chloride by 100 gm soil mixed with 5-10 gm chalk. But he was unable to explain his results in the ordinary chemical way and obviously, although he came to the conclusion that high fertility went hand in hand with the degree of absorption, the results he obtained for different soils were not strictly comparable. He employed a dilute /

dilute solution, and the addition of chalk complicated matters so that the method really gave a badly defined quantity.

Pillitz (78) modified the Knop method by omitting the addition of chalk and leaching the soil with concentrated ammonium chloride solution until equilibrium was reached. His method certainly brought about complete replacement and gave what he called an "Aussätigungspunkt", but he did not determine the bases replaced and assumed that the absorption occurred after the conversion of the ammonium chloride into ammonia by the soil carbonates.

Kellner (59) examined several soils, free from carbonate, bythe Pillitz method and determined in one case the bases released as well as the ammonium absorbed. However, one experiment in which he attempted to measure the absorption of calcium from calcium chloride after saturating the soil with calcium hydroxide, indicates that he had no clear idea of the nature of the phenomenon.

Way had suggested that it was necessary to isolate the absorbent substances and study their properties in a less complicated condition if material progress were to be made. It was not however until 1870 that Lemberg (61) commenced his notable series of experiments on the equilibrium after base exchange in the case /

case of pure silicates, and demonstrated that the reaction was reversible and that there was an equivalent exchange of bases. Then Armsby (2) after working with artificial silicates and calcium chloride introduced the conception of an equilibrium mixture. He found that the exchange of bases was only partial and varied with the concentration of the solution and the ratio of soil to solution, and came to the conclusion that it was probably due to action of mass or reversible reaction.

APPLICATION of COLLOIDAL CHEMISTRY.-

Lemberg's work has been considerably extended in the last twenty years with the preparation of artificial silicates or permutites and their conversion into various compounds by base replacement for industrial purposes, but it was van Bemmelen (3,4,5,), who opened up a fresh method of attack on the question of soil absorption. The subject of colloid chemistry was occupying a great deal of attention and van Bemmelen devoted his time to the investigations of substances in colloidal state and particularly the behaviour of absorption compounds or compounds of inconstant molecular proportions. He worked with pure colloids and with mixed colloids and measured the absorption of bases, acids and salts. He observed that the combination of bases with silicic acid gave compounds /

compounds which could undergo reversible exchange of bases and suggested that the mechanism of a reaction between solicic acid, which had absorbed CaO, and KCl might be

$$\begin{matrix} 2\,K & 2\,Cl \\ Ca & 2\,(OH) \end{matrix} \longrightarrow 2\,KOH \text{ absorbed leaving } Ca^{\cdot\cdot} \text{ and } 2\,Cl^{\prime} \text{ in solution.}$$

He dealt with the question of quantity of absorbent, initial and final concentrations, effect of temperature, velocity of absorption and influence of other factors. His chief conclusions in 1888 were:- Whether the absorption gave a homogeneous compound or was merely a surface concentration, was undetermined except in the case of crystalline silicates where chemical compounds were undoubtedly formed; the absorptive power depended upon the molecular state of aggregation, varied for different substances absorbed and decreased as amount absorbed increased; the relationship between absorption andequilibrium concentration was a function of the concentration and temperature but obscure; the soil contained silicates, iron oxide, silicic acid and humus substances in colloidal condition, all of which might play a part in absorption. He allowed the whole question to appear in a new light by demonstrating that the active substances in soil absorption were substances in colloidal condition with a large surface development.

Those new ideas were responsible for a great deal of work covering the absorption of solids, liquids and gases /

gases by substances in a state of fine division, the rate of absorption and the introduction of formulae to represent the energy changes and the distribution of solute between solvent and absorbent. Patten and Waggaman (74) have dealt very fully with the literature of that period and it is unnecessary to do more than sum up the position ten to twenty years ago. Commenting upon the condition of the absorbed substance those authors discuss the possibility of concentration changes in a two phase system in virtue of the surface tension between solid and liquid and of chemical combination at the surface of the solid. But they acknowledge the complications involved when a soil is the absorbent, due for example to the modifying factors introduced by flocculation (15) or change in physical structure, and they state "all gradations of union are possible, from purely physical surface adhesion (which still depends upon the composition of the bodies involved) to purely chemical combination. One important intermediate step may be solution, either liquid or solid".

The experimental work at that time usually involved the determination of the initial and final concentrations, the relationship being expressed by the Freundlich equation

$$\frac{x}{m} = \beta . c^{\frac{1}{p}}$$

where β and p are constants varying with the conditions, x is the quantity absorbed, m the amount of absorbent /

absorbent, and C the equilibrium concentration. That equation has been employed to express and explain innumerable results obtained in soil investigations but perhaps the most exhaustive application of the method to the subject of base exchange was made by Wiegner (103) with an artificial calcium permutite investigated previously by Gans (28). Carrying out experiments with ammonium chloride solutions he found that equilibrium was reached very quickly, that the absorption decreased only slightly with rise in temperature between 5°C and 50°C, that the state of mechanical division of the silicate did not have much influence but that dehydration and then ignition reduced the absorption to zero. He showed that the exchange was confined to the cations and that the calcium and potassium liberated were together always greater than the equivalent ammonium absorbed. That he ascribed to the production of NH_4OH from the ammonium silicate formed to provide sufficient OH ions to balance the excess of cations in solution. He expressed his results quantitatively by equations which had been employed for adsorption reactions and concluded that the Freundlich equation was best suited; but it is interesting to observe the empirical nature of the equation revealed by the fact that $\beta = 3.429$ and $1/p = .398$ dealing with concentrations $\frac{N}{30}$ to $\frac{N}{3}$, while $\beta = 2.823$ and $1/p = .336$ when the experiment is /

is extended to concentrations of 5 N He also calculated the results of Henneberg and Stohmann and of Armsby to show that they also fall into line with this idea of an adsorption isotherm, and he submitted that β gave a measure of the absorption of any cation.

While admitting that the equivalence of the exchange suggested chemical reaction Wiegner regarded the Law of Mass Action as inadequate to explain the facts quantitatively in so far as the composition of a substance of constant composition should be independent of the concentration of the solution. Discussing the possibility of the solute forming a solid solution with the absorbent on the basis of the Nernst Distribution Law he showed that the absorption should be proportional to the concentration if the molecular state remains unaltered, and was forced to revert to the hypothesis of van Bemmelen involving absorption compounds. Since typical adsorption isotherms could be obtained he contended that there was justification for explaining the mechanism in terms of capillary forces. The capillary spaces were decreased by dehydration and destroyed by fusion. He suggested that OH ions were adsorbed by the positively charged colloid $Al(OH)_3$+ $Si(OH)_4$ and cations equivalent in amount concentrated in the gel water to give the amorphous "Doppelsilikate mit Austauschvermogen". These /

These bases were held electro-chemically. On addition of a neutral salt to the gel the cations present re-distributed themselves according to their "adsorbierbarkeit" but the OH ions were so strongly adsorbed that the anion was not affected. Incidentally the firm binding of the OH ions accounted for the insignificant action of pure water in liberating the bases from a substance capable of base exchange. It is unnecessary to dwell longer upon the matter because Wiegner has modified his views since 1912. The important fact which emerged from that work was that the same phenomena had been observed with soils varied alike in their physical and chemical nature, so that the basis of cation exchange in the soil seemed to be the same as, or at least closely allied to, that in those double silicates. About the same time Aberson (1) expressed the same opinions after experimenting with ammonium chloride and soils, and it is of interest to note that he found that the absorption by a soil was lowered after treating it with exchangeable ions.

MODERN VIEWS.-

Meantime many soil workers, especially in America, had turned their attention to the cause and nature of soil acidity. Since the question of soil acidity is now intimately linked up with that of base exchange /

exchange it seems necessary to refer briefly to the theories that were advanced. In 1902 Clarke and Stieger (18) indicated that the composition of silicates is such as to admit of base exchange and that the acid salts of the various silicic acids might contain replaceable hydrogen. Cameron (16) was one of the first to attribute the acid reaction of a soil to selective ion adsorption rather than to the presence of acids other than carbonic acid, and Harris (41,42) published several papers in support of that idea of regarding the acidity of a salt solution extract of a soil as due to fixing of the base and liberation of acid. Sullivan (92) and also Hall and Gimingham (40) had suggested the possibility of exchangeable iron and aluminium, their salts being hydrolysed, but E. G. Parker (73) believed that partial hydrolysis of the salt added took place first, its extent depending upon the nature of the anion and determining the amount of adsorption, the solution of weak bases and the resultant acidity. Truog (97) discussed the probable mode of formation of acid soils by weathering, and maintained that acid mineral substances might be produced. Organic matter might also, under certain circumstances, give rise to acid conditions, the determination of which was complicated by secondary reactions. He drew attention to the fact that a great /

great many chemical reactions proceed only to partial completion depending upon the concentration and solubility of the reacting substances, and exhibit the same kind of equilibria relationships as adsorptions, so that soil absorption is not necessarily an adsorption He went so far as to say that the acid reaction of a soil is due to chemical nature rather than colloidal condition.

Later work* dealing with the H-ion concentration of acid soils and Bradfields' investigations (9,10,11) on clay, coupled with the present tendency (71) of regarding humus as containing a mixture of organic acids of high molecular weight, indicate that there is little room for doubt that acid substances are actually present in sour soils. That being so, it naturally follows that hydrogen may be regarded as playing a rôle similar to that of the exchangeable bases, the acidity of a salt solution extract of a soil being due to the hydrogen replaced from the soil by the cation of the salt. Whether the exchange is a case of simple double decomposition or is the result of some physical phenomenon followed by a chemical reaction seems to be a matter for secondary consideration since the views on the nature of the change, which are now generally accepted, would appear to be adequate to explain and predict the results obtained in soil investigations.

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* See References, 83, 84, 37, 49, 50, 77, 26, 20, 48.

It was recognised at an early date that most soils possessed similar properties differing only in degree, and it was natural that attempts should be made at classification. Glinka's broad generalisations on the question of soil types, modified in certain cases to meet different conditions provide a satisfactory working hypothesis. His views [37a] may be summed up as follows: The chief properties of a soil arise from the actual processes of its formation, which may largely efface the mineralogical, mechanical and chemical differences in the parent rock; that is to say, climatic factors play the chief rôle in effecting changes in the organic matter, decomposition of the mineral substances and redistribution of the products, and often give rise to types closely related to the climate of the region in question. The facts seem to bear out this contention in dealing with mature soils which have been subjected to prolonged weathering and have reached a stage of pedological equilibrium, but Hendrick and Ogg [43] and Hendrick and Newlands [44,45], from mineralogical studies of the fine sand from a number of British Soils, have pointed out that that climatic basis for classification is not altogether applicable in the case of immature soils. Such soils arise mostly from glacial drift formed mainly by mechanical processes, and contain considerable amounts of silicates which have been little /

little altered chemically - the post-glacial period having been too short to affect the mineral composition to any great extent except in the case of readily decomposed material. Rocks unlike in composition may therefore give rise to soils unlike in character. At the same time the climatic differences, even in a country the size of Scotland, are sufficiently great to account for the same geological formation giving rise to different soils (70). But in either case the soil does not consist merely of finely divided rock material but "of more or less decomposed rock and mineral particles of varying sizes associated with a hydrated colloidal complex of clay and organic matter which we conceive as a kind of matrix investing the particles .... " (86). That that colloidal complex is responsible for the characteristic physical and chemical properties of a soil is indicated by such investigations as that of McCool and Wheeting (64) on soils from which the colloids had been removed, but how it is formed is a matter of speculation. The formation is undoubtedly a secular process giving rise to substances of inconstant composition, and if, as suggested by Glinka, inter alia, the breaking down of the silicates is a progressive hydrolytic process produced by the action of heat, water and carbon dioxide, then the complexes may be formed by mutual precipitation of the resultant colloids, as indicated by /

by Gedroiz. The last mentioned worker, after a most exhaustive study (29 - 36) of Russian soils, suggested two possible modes of formation of that complex which is capable of cation exchange. On the one hand, since the property of exchange is confined to finely divided particles it may arise simply through mechanical and chemical weathering to give particles which will ultimately be dispersed to such an extent as to possess that property. On the other hand, the complex may be a new formation due to mutual precipitation of the colloidal hydroxides produced by weathering. The precipitated mixed gels will carry down with them from solution cations including hydrogen, and in virtue of their large surface area will play a most important part in the life of the soil. Both processes however may take place.

In 1916 Gedroiz showed that cation exchange was reversible, that all the exchangeable bases in a soil could be replaced by any one base, and that a soil, saturated with any base, contained it in a quantity independent of the nature of the base. His methods, results and conclusions will be dealt with more fully at a later stage but it is convenient to indicate here his ideas on the subject in 1918-19. He dealt fully with the "Energy of Absorption and Replacement" of different cations and showed how it depended upon the previous state of saturation of the soil colloids with the /

the cation in question; a fact neglected by other workers and leading to many inaccurate generalisations on the absorption of bases. He also introduced the term "Volume of Absorption" to denote the maximum quantity of bases which might be present in an absorbed and exchangeable condition, a characteristic and definite quantity for any soil. A soil containing that maximum amount of bases is saturated whereas, if its content of exchangeable bases is less than that amount, it is unsaturated. Furthermore it can be determined only by direct replacement of the bases, the results obtained by analyses of hydrochloric acid extractions being sometimes quite misleading.

It is noteworthy that Hissink (47, 96), after investigations extending over many years, arrived at almost the same conclusions as Gedroiz. Hissink has introduced the term "Sättigungszustand" to describe the ratio of S, the absorbed bases present in the soil, to T, which is actually the "Volume of Absorption" of Gedroiz, and has pointed out how there may be a continuous succession from soils completely saturated with bases, to soils completely unsaturated. He has discussed at length the relationship between acid soluble bases and exchangeable bases, has made an attempt to explain the mechanism of base exchange and, like Gedroiz, has laid great stress upon the influence which those bases exert on soil behaviour. It is convenient /

convenient to leave the question of the mechanism of the reaction for later discussion, but it would appear advisable to submit at this point the facts for which we are indebted to those investigators.

They have both shown that the content of exchangeable bases in a soil depends in the first place upon the quantity of absorbing material, mineral and organic, and in the second place upon the age of the soil and its history. They have emphasised, in addition, the tremendous importance of the nature of the exchangeable bases. The presence of significant amounts of univalent bases confers on the soil the properties associated with semi-reversible colloids, viz. plasticity, swelling, and so on leading to deterioration of the soil structure. On the other hand the bivalent ions promote the formation of amorphous gels which give rise to a crumbly structure with good porosity, drainage and circulation of air and heat. Unsaturation, or the replacement of exchangeable bases by hydrogen, also disturbs the colloid chemical equilibrium and the absorbing complex may cease to function as a hydrogen regulator, with bad effects on both physiological and bacteriological processes. They both considered that the rapidity of exchange was such as to justify regarding the action as a surface one, the exchangeable bases being concentrated on the surface of the active complexes. In 1918 Gedroiz regarded the /

the nature of the combination between complex and cation as essentially chemical but a few years later (1922), in considering the different forms of absorption, he draws a clear distinction between chemical absorption involving precipitation of the anion of a neutral salt and physico-chemical absorption involving only mutual exchange of cations. He also distinguishes physico-chemical absorption, which leaves the concentration of the solution unchanged, from physical adsorption which changes that concentration. In chemical absorption cation exchange is followed by precipitation of an insoluble salt, in physico-chemical absorption the cation absorbed passes into a solid condition and can be extracted only by replacement or decomposition, in physical adsorption the substances absorbed may be washed out by the action of water. Hissink is inclined to look upon base exchange as a phenomenon totally dependent upon the affinity of the absorbing complex for different ions, the only difference from reaction in true solution being due to the presence of a solid phase. When the size of the particles approaches molecular dimensionsthen one may expect to finda close analogy to an ordinary chemical reaction, and the fact that the humus appears to absorb and exchange about twice as much as the mineral fraction would bear that out since the former has usually a greater specific surface than the latter.

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Such a hypothesis certainly accounts for the equilibrium relationships which are found, avoids the necessity of having recourse to purely physical phenomena for an explanation and brings the question in to the same category as other heterogeneous systems. It provides an explanation of the phenomena observed for example by Brustlein (12) and van Bemmelen (3) regarding the action of hydrochloric acid in destroying the power of a soil to absorb from neutral salts and the effect of carbonates and hydroxides in restoring that power. It is unnecessary to look upon calcium carbonate as essential to convert the salt into hydroxide as suggested by the former, or into carbonate as suggested by the latter. The acid treatment may be regarded as partially destroying the exchange complexes and partially replacing the exchangeable bases by hydrogen to give acid complexes. The hydrogen is so firmly held that ordinary treatment with neutral salts is insufficient to produce a recognisable exchange of the hydrogen and the cation in question. The presence of a carbonate or hydroxide however may be regarded as bringing about a simple action between acid and base, with the production of water, and a complex containing an exchangeable cation and now capable of entering into base exchange with the cation of a neutral salt.

The equilibrium set up on adding a salt solution to /

to a soil may be continually pushed in one direction by removing the soluble products and adding fresh solution or by leaching; eventually all the exchangeable ions originally present are replaced by the cation of the salt. The H-ion concentrations of the soil and solution, the anion of the salt and the energy of replacement of its cation, will all play a part in the process, but the important point is that the absorptive capacity or volume of absorption at any particular time is a definite and characteristic quantity for any soil.

OBJECT of this RESEARCH.

The importance of the subject of Base Exchange as a means of grouping together so many known facts on absorption has excited tremendous interest. That is revealed by the reports of the Second International Commission, Rome 1924, and by the discussion on Base Exchange at the Faraday Society, London, 1924, without making reference at present to the many publications of individual workers both in Europe and in America. The object of this research was:- To determine the exchangeable bases in a number of soils in the East of Scotland: to note how the results obtained varied from soil to soil and compared with the data submitted by other workers: to consider the relative proportions of the different exchangeable bases and investigate the changes which might be effected by means of neutral salts in order to ascertain what differences, if any, might arise in the application of the same manurial treatment to different soil types: to attempt to correlate the facts and indicate those lines along which further research might be carried out to best advantage.

PRELIMINARY EXPERIMENTS.

ABSORPTION from AMMONIUM SULPHATE SOLUTIONS by SOIL 196.

The experiments to be described were intended to give some indication of the absorption properties of one of the soils to be more fully examined later. Soil 196 was obtained from what had been a plantation of trees at least fifty years old. The surface soil contains a considerable amount of undecomposed organic matter and is loamy, whilst the subsoil is lighter in colour and becomes sandy at 18 inches - really a gravel mound. The reason for taking such a soil was that it could not have received artificial treatment for a long time so that the results were not likely to be influenced by recent additions of fertilisers. The percentage loss in weight at 100°C - 105°C was 9.94, and the loss on ignition amounted to 10.98 per cent. Other data will be found in table 7.

PERCOLATION EXPERIMENT.

The following experiment was designed to show in a qualitative manner the rate of absorption and leaching. A glass tube 1" diameter was drawn out at one end at which was fitted a porcelain filter, and 100 gm. soil were packed in and occupied 9"-10". A solution of ammonium sulphate containing .1672 gm NH_3 per 100 c.c. was poured in at the top of the tube and the percolate, which came through at the rate of 100 c.c. in /

TABLE 1.

RATE OF ABSORPTION AND LEACHING.

Flask	Percolate.		
	Volume in c.c.	Colour	gms. NH_3 per 100 c.c.
i	100	very slight.	.1145
ii	100	" "	.1562
iii	100	" "	-
iv	100	" "	.1613
v	100	" "	.1639
vi	50	" "	.1546
vii	50	brownish-yellow	.0474
viii	100	" "	-
ix	250	" "	-
x	250	" "	-
xi	250	" "	.0004
xii	250	" "	.0001
xiii	250	reddish-brown	-
xiv	500	" "	-

in 15 minutes, was collected in separate flasks and analysed. It will be observed (table 1) that the absorption rapidly decreased and that equilibrium had almost been attained after 500 c.c. had been collected. At that stage no more solution was added, and, after allowing the tube to stand a week distilled water was added. Percolation recommenced immediately and the first few c.c. were very brown in colour; the percolate then became straw-coloured. After that the percolation was very slow. The excess ammonium sulphate in the soil was almost completely removed by leaching with 1200 c.c. of distilled water. The replacement of other bases by ammonium and the washing out of excess soluble salts apparently led to considerable deflocculation of the soil colloids as shown by the very slow rate of percolation towards the end and the dark colour of the percolate. That point will be discussed later.

ABSORPTION EXPERIMENTS.

(a) Absorption of Cation.

In these experiments a weighed quantity of soil and a measured volume of ammonium sulphate solution were placed in a bottle and agitated for between two and three hours on an end-over-end shaker. After being allowed to settle over-night the supernatant liquid, which usually remained turbid even after standing several days, was filtered through a small wool /

wool plug the first few e.g. being discarded. For each determination of NH_3 a convenient amount of the filtrate was pipetted off into a hard glass flask, diluted to about 300 c.c. and distilled with caustic soda. The distillate was collected in standard sulphuric acid and titrated in the usual manner with standard sodium hydroxide using methyl red as indicator.

The probable error of any one analysis calculated from nine determinations of $\frac{K}{10}(NH_4)_2 SO_4$ solution by the method of least squares, is .4 per cent, and the fact that almost identical results were obtained whether the time allowed for settling was one day or several days indicated that the absorption was complete under the conditions and that the degree of turbidity did not influence the result to any extent. Centrifuging the filtrate to obtain a clear solution was tried but evaporation was found to take place and very low results were obtained. The results are collected in table 2, each figure in columns 3 and 4 being obtained from at least two determinations in close agreement. The soil contained about .006 per cent of water soluble NH_3. The absorption in experiments 1 and 3 is so small that the results are not reliable, but considering the other results it will be seen that the absorption of NH_3 by soil 196 is not great. Experiment 20 was carried out with soil 385 (see table 4) and is quite comparable with experiment 8, whilst /

TABLE 2.

ABSORPTION OF NH_3 BY SOIL 196.

No.	gm. Soil per 100 c.c.	gm. NH_3 in 100 c.c.		gm. NH_3 absorbed	
		Before	After	from 100 c.c.	by 100 gm. Soil.
1	10	·1686	·1650	·0036	·036
2	14·3	·1686	·1608	·0078	·054
3	7·2	·1686	·1650	·0036	·050
7	25	·1672	·1509	·0163	·065
8	30	·1668	·1476	·0192	·064
9	25	·827	·787	·040	·160
10	25	·0817	·0726	·0091	·036
11	50	·0817	·0651	·0166	·033
12	50	·0817	·0650	·0167	·033
13	50	·0817	·0655	·0162	·032
14	25	·1668	·1517	·0151	·060
20	30	·1667	·1416	·0251	·083
A.	50	·085	·057	·028	·057
B	a. 30	·013	·006	·007	·023
	b. 40	·103	·035	·068	·170

whilst A and B are results obtained by Henneberg and Stohmann (46) and by Weinhold (101) respectively. All three soils appear to have a greater absorptive capacity than 196.

Wiegner (103) amongst others has dealt with the effect of temperature on absorption and pointed out that, although the conflicting and varied statements may be due to the complexity of the problem and apparent contradictions may be due to different combinations of factors, the actual influence is insignificant. In experiment 12 the treatment of soil with solution was carried out in a thermostat at 26°C. Otherwise the experiment was exactly the same as number 11 and the results obtained are within experimental error.

Karpizov* found the absorption to be a maximum with the surface soil and to decrease towards the subsoil. Experiments 13 and 14 were carried out with soil from a depth of 9"-18" and are comparable with 11 and 7 respectively. The absorption by surface soil is greater in each case. With soil 196 that was to be expected since the content of fine particles decreases with depth but of course the result is not applicable to any soil type.

The experiments carried out do not furnish sufficient data for purposes of generalisation but the well known facts on absorption are borne out.

In /

*Abstract Experiment Station Records 16,652.

In the first place experiments 7, 10, 9 show that when the solutions are dilute there is a rough proportionality between the concentration and absorption but that when more concentrated solutions are employed the proportionality disappears, the absorption increasing much more slowly than the concentration. In the second place an increase in the ratio soil: solution, caeteris paribus, brings about an increase in the absolute absorption but, if anything, a decrease in the relative absorption: compare experiments 7 and 8 with $\frac{N}{10}$ solution and experiments 10 and 11 with $\frac{N}{20}$ solution. Finally experiments 7 and 11 show that 25 gm soil absorb almost the same amount from 100 c.c. $\frac{N}{10}$ solution as 50 gm absorb from 100 c.c. $\frac{N}{20}$ solution, a further indication of the rough proportionality existing between quantity of absorbent and concentration of solution when the solutions are dilute.

(b) Absorption of Anion.

It is usually agreed that the anion is not affected by the absorption changes in a neutral salt solution, unless it forms an insoluble compound with one or more of the bases replaced. When the salt is ammonium sulphate there is a possibility of calcium sulphate being precipitated. Sulphate determinations were made on a number of the solutions analysed for NH_3, and the results are recorded in table 3. It will be seen that except in experiment 9 the SO_4'' absorbed

was /

TABLE 3.

ABSORPTION OF SO_4 BY SOIL 196.

No.	gm. SO_4		gm. NH_3	
	in 100 c.c. before	absorbed from 100 c.c.	equiv. to SO_4 absorbed	absorbed from 100 c.c. Table
8	.470	.014	.005	.0192
9	2.360	.112	.039	.040
10	.2319	.0041	.0014	.0091
11	.2319	.014	.005	.0166
12	.2319	.011	.004	.0167
14	.470	.008	.003	.0151

was much less than the NH_3 absorbed but much greater than experimental error which was less than .2 per cent. The solubility of calcium sulphate is about 1.5 gm per litre in the ammonium sulphate solutions employed * and soil 196 contains about .03 per cent exchangeable calcium (p. 50). It is obvious that in no case could the calcium liberated be sufficient to account for the reduction in sulphate. Of course secondary reactions might occur in such a complex mixture but, as Gedroiz has suggested (33) there is no reason why a soil should not have an absorptive capacity for anions, as it has for cations, and it may be so small or completely saturated with the anions in the soil solution in most cases that there is no measurable absorption of those anions. The problem however lay outside this investigation and was temporarily set aside.

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* Siedell. Solubilities.

THE EXCHANGEABLE BASES.

Attention has already been drawn to the stress laid by many investigators on the very important rôle of the exchangeable bases in matters affecting the structure of the soil and its chemical and biological properties. At present there seems to be no doubt that the exchange process involves an equilibrium and that early work in this field loses a certain amount of its value because that was not recognised. The data collected resulted from partial rather than complete replacement because the soil was usually shaken up with a solution of a salt and the changes in concentration or composition of the liquid determined as in the preliminary experiments already described. Complete exchange was not possible although, when concentrated solutions were employed, the reaction may have proceeded a considerable distance. Furthermore the absorption depends upon the quantities of soil and solution employed and no information regarding the proportions of the previously absorbed bases is obtained. Only by treating a soil repeatedly with fresh quantities of a salt solution can all the exchangeable bases be replaced and one of the most important points established is that the content of those bases is a definite quantity for any soil and independent of arbitrary conditions of determination. The twenty soils described in /

in table 4 were leached with a normal solution of ammonium chloride and the bases replaced were determined. Hydrogen is difficult to replace completely, especially by a limited quantity of a univalent cation, and the leaching was carried on only until the calcium replaced became negligible in amount. Gedroiz usually extracted the exchangeable bases by a method analogous to repeated washing by decantation and found the exchange process to go on for a long time. Hissink on the other hand leached the soil, and his method was adopted as being the quicker and more economical.

Fig 1. East of Scotland

THE SOILS EXAMINED.

Fig. 1. is a sketch of the coast line and will show at a glance where the soils were obtained. In every case, unless otherwise mentioned, the material examined was the surface layer and belonged to the A horizon. Information on the soil type, where it was sampled and the geological formation, is collected in table 4.

The first seven soils are from the Edinburgh and East of Scotland College Experimental Farm at Boghall, 5 miles south of Edinburgh. The hillside soils 170, 386, 417 overlie basalt rocks of Old Red Sandstone Age, but 178, 196, 385 are on the flat and approach closely to the inferred position of the fault between Old Red Sandstone and Carboniferous rocks. 196 and 386 are from uncultivated ground, the former (see p. 25) being from an old plantation recently cut down, the latter from a part of the hillside about 1000 feet above sea level.

A full description of the profiles of the types mentioned has not been published yet but the following notes are sufficient to indicate the differences existing in the field conditions of those soils.

Boghall 15. A reddish or chocolate coloured loam to gravelly sandy free working loam: subsurface friable and only moderately compact and retentive passing into dark compact drift clay relatively impervious.

Drainage /

TABLE 4.

THE SOILS EXAMINED.

No.	Type	Location and Geological Formation.
169	Boghall 15	Boghall, Basalt nearest rock in situ.
170	" 20.	" , Basalt.
178	" 35	" , near inferred position of fault separa Carboniferous from Old Red Sandstone.
385	" 42	" , field running alongside 196. See 178
196	" 8	" , plot uncultivated for at least 50 yea See 178.
417	" 37	" , field within area of Residual Basalt.
386	" 39	" , uncultivated hillside above 417.
243	Gladsmuir Loam 39	Pencaitland, E. Lothian. Carboniferous Limest
247	" " "	" " " "
276	Dunbar Loam 3.	Dunbar, " Old Red Sandstone.
277	" " 1.	" " Calciferous Sandston
290	Perth 7 admixture Gladsmuir Loam 29	Kirkcaldy, Fifeshire. Permanent Pasture. Dol
331	Lammermuir 12	Galashiels, Selkirkshire. Grits of Lower Silu
332	" 8X	" " " " "
337	Boghall 39 admixture Winchburgh 51.	Linlithgow. Basic Volcanic.
343	Carse of Stirling	Alva, Clackmannanshire. Overlying Carbonifero but most probably related to Old Red San stone Basalts.
355	Perth 3	Perth. Old Red Sandstone.
358	Carse of Gowrie	Carse of Gowrie, Perthshire. Typical carse la pasture at least 40 years.
398	Insch group	Insch, Aberdeenshire. Drift derived from basi igneous rock. *
399	Aberdeen group	Craibstone, Aberdeenshire. Granite drift. *

* For samples of these soils I am indebted to Professor Her and Mr. G. Newlands, who have described them more fully in a paper dealing with the mineralogical examination of soil types. - J. Agri Sci. 1923. 13.pl.

Drainage good. A fluvio-glacial deposit rich in basic igneous volcanic rocks on bed of boulder clay.

Boghall 20. A chocolate and brown loam moderately compact and coherent overlying a lighter coloured plastic gritty clay moderately impervious and retentive. Surface drainage fair to good, internal fair. Probably belonging to a widespread group of soils of good agricultural value. Material largely basaltic and andesitic.

Boghall 35. A brown slightly coherent fine sandy free working loam passing into a lighter coloured loosely coherent fine sand extending 2 or 3 feet and overlying boulder clay. Distinguished from Boghall 15 and 8 by higher percentage of fine and medium sand and less gravel, silt and clay. Drainage good - not excessively droughty.

Boghall 42. A brown loam or sandy loam capable of becoming compact: subsurface - loam or sandy loam passing into sandy clay: Surface drainage fair to poor, internal drainage poor with water logging.

Boghall 8. Profile similar to Boghall 15 but distinguished by higher percentage of sand and gravel - reddish colour not strongly marked. Free drainage - probably suffers from drought. Sample taken from what appears to be a virgin profile and surface material has high content of organic matter.

Boghall 37. Profile similar to Boghall 20 but marked by /

by presence of larger stones and higher percentage of coarse gravel although not sufficient to produce an open pervious structure and free drainage. Elevation 700 feet. Shown on geological map as residual basalt but probably a thin layer of coarse ice-laid deposits with outwash. Largely basaltic material.

Boghall 39. A dark brown degraded peatty layer (3-5 ins.) overlying a reddish brown gravelly and pervious loam only moderately retentive, passing into a mass containing silt and clay as interstitial matter; then shattered rock (mainly volcanic basalt and andesite) with less clay on bed rock at 12-40 inches. Good drainage throughout. Elevation 900-1600 feet.

Gladsmuir Loam 39. A brownish friable not excessively coherent loam passing into a lighter brown (in places yellowish and greyish mottled) friable loam with limonitic accretions: then a yellowish to chocolate or liver coloured moderately compact layer with high percentage of rock fragments resting directly upon bed-rock of shale and limestone at 2-4 feet. Surface drainage good, internal drainage fair but not excessively cold and wet.

Dunbar Loam 3. A brown light friable loam passing into a yellowish brown more compact layer 18 ins. thick and then a brown fairly friable clay material resting upon basal Old Red conglomerate.

Dunbar Loam 1. A reddish friable light loam pervious but /

but fairly retentive passing into a lighter shade and then a more vivid red compact gritty moderately pervious horizon with appreciable influence of limestone. Drainage good. A rich arable soil.

Perth 7. A dark brown loam friable and crumbly despite high content of silt and clay: Subsurface an ill-defined brown layer and than a lighter coloured heavier but still crumbly layer resting on rock.

Gladsmuir Loam 29. A greyish or yellowish brown loam capable of becoming compact: lower horizons range from yellowish to reddish and chocolate with some mottling of colours and are plastic in consistency: substratum a stiff gritty clay relatively impervious and retentive. Drainage fair at surface, becoming poor with depth. A widespread type in central Scotland.

Lammermuir 12. Plough soil a light yellowish brown or grey silty loam resting on yellow or buff or reddish yellow material full of slate, shale or graywacke fragments; then shattered bed rock. Drainage, surface fairly retentive, internal free water movement. A glaciated surface with a characteristic small thickness of soil over the rock.

Lammermuir 8X. A brown to reddish brown gravelly loam or sandy loam, yellowish to reddish in B horizon. Loose pervious structure throughout profile. Large percentage of gravel and stones as graywacke and slate, interstitial silt imparting a greasy feel.

Winchburgh /

Winchburgh 51. A dark brown loam coherent and slightly sticky when wet, passing into a yellowish sandy loam containing occasional segregations of black iron oxide, then a chocolate coloured gritty but moderately plastic and highly retentive ice-laid clay with shale influence predominant. Drainage: surface fair to poor, internal poor. Probably an extensive type in central Scotland - especially West Lothian - and closely related to Gladsmuir Loam 29.

Carse of Stirling. A greyish brown silt loam sticky and greasy when wet, overlying a fine silty layer lighter in colour and about 1 foot thick; then a grey and yellow mottled heavy layer resting at 4 feet upon the parent material - a bluish fine silt or clay, very plastic and sticky.

Perth 3. A fairly heavy brown loam derived from boulder clay with no marked change to depth of 2 feet: substratum sandy with some interstitial clay. Allied to Dunbar Loam 3 but probably admixture of volcanic material. Drainage good throughout profile.

Carse of Gowrie.(Lower flood plain). A brownish humus layer passing into a yellowish fine silt and then a mottled grey and yellow clay 2 feet in thickness and overlying a grey fine silt many feet thick. The parent material is probably not so dark in colour as that of the Stirling Carse type.

Insch /

Insch Group. A brown friable loam passing into a yellowish brown sandy material and then a layer of coarse particles of decomposed rock full of mica and pyroxenes resting upon rock - olivine norite.

Aberdeen Group (intermediate type). A brown light loam: a virgin profile consists of a layer of peat overlying a brownish yellow layer showing incipient pan formation at about 7 inches under which is a yellow ochre gravelly loam 15-20 ins. thick. The soil examined (399) was not from a virgin profile.

METHODS.

The soils were air-dried at laboratory temperature and passed through a 3 m.m. sieve. Qualitative tests showed that they contained neither free carbonate nor water-soluble salts except in minute traces.

The pH of each soil was determined by means of the quinhydrone electrode(6). 10 gm. of soil, a few decigrams of quinhydrone and 50 c.c. water were shaken by hand for about one minute and poured into a beaker. A polished platinum electrode was placed in position, connection was made with a ·1 N calomel electrode, and the voltage read off on a potentiometer. The results have been given to the second decimal place, but it is desirable to observe that, although the error is of the order ·03 as pH and the measurements are reproducible in any particular soil sample, such accuracy is unnecessary and apt to be misleading in view of the many disturbing factors which may arise in working with soils.

The "Lime Requirement" was determined after the manner described by Hutchinson and MacLennan(53). 20 gm. soil and 300 c.c. ·023 N Ca $(HCO_3)_2$ were shaken for 3 hours and the filtrate titrated with ·2 N HCl using methyl orange as indicator. The pH value and the "Lime Requirement" as $\%CaCO_3$ are included in table 7 for the sake of ease in comparison with the other /

other data. The loss at 105° C, returned as moisture and the loss on ignition, which may be regarded as organic matter in view of the absence of carbonate and the small content of clay, are also included in table 7.

Hissink (47) has demonstrated that when calcium carbonate is present in a soil, leaching removes more calcium than is present in exchangeable form, and while sodium chloride dissolves calcium carbonate in amount proportional to the leaching, ammonium chloride dissolves quantities which depend upon the content of carbonate present. The question does not arise here and since the use of ammonium chloride is obviously essential in the case of potassium and sodium, that salt was employed throughout.

To extract the exchangeable bases, 25-30 gm. soil were stirred, at intervals, for an hour with about 100 c.c. warm N. NH_4Cl solution. After standing overnight the supernatant liquid was decanted on to a filter and allowed to drain, the residue being stirred up with 50-100 c.c. cold N. NH_4Cl. The supernatant liquid from this was in turn poured on to the filter and the process repeated until the filtrate amounted to 500 c.c. By this means the soil had been brought into contact with at least seven or eight fresh lots of NH_4Cl so that the basic exchange could be regarded as complete without serious error. The extraction was continued until a second half litre had been /

been collected.

While admitting that equilibrium is reached very quickly the preliminary warming and stirring is necessary in some cases to ensure that the soil is thoroughly wetted and put into a condition suitable for maximum exchange.

Iron, aluminium, calcium and magnesium were determined in each half litre. The iron and aluminium were precipitated together by boiling the solution with a little ammonia. The precipitate of mixed hydroxides was filtered off and ignited in the usual manner. The mixed oxides were then fused with potassium persulphate and the iron in the extract determined volumetrically with $\frac{N}{50}$ permanganate after reduction by stannous chloride. The tervalent bases were obtained from only three soils and being in practically equal amounts by weight have been returned as $Fe_2O_3 + Al_2O_3$. Further reference is made in appendix 1 on page 76.

To determine the calcium the solution was made slightly acid with hydrochloric acid and heated to boiling point. About 10 c.c. of a boiling 2 per cent. solution of ammonium oxalate were slowly added, then ammonia until the solution was decidedly alkaline, and boiling was continued until the precipitate of calcium oxalate became granular. After standing on the steam bath for 90 minutes the solution was filtered and the calcium determined volumetrically.

The /

The filtrate was evaporated to dryness and the ammonium salts were volatilised by gentle ignition. Any silica present was then separated, and the magnesium rendered soluble, by taking to dryness at 100°C with hydrochloric acid, extracting with water and filtering. Any traces of iron, aluminium or calcium were eliminated by treating the solution with small quantities of ammonium chloride, ammonia and ammonium carbonate and filtering; that treatment also served to flocculate organic matter. The magnesium was precipitated in neutral solution at boiling point with microcosmic salt; after cooling, the solution was made strongly ammoniacal, stirred vigorously and allowed to stand overnight. The precipitate was filtered off and ignited apart from the paper, the magnesium being weighed as pyrophosphate.

Potassium and sodium were determined in the first and second half litres obtained from another extraction. To get rid of the ammonium chloride the solution was at once taken to dryness and gently ignited. The residue was extracted with hot water and filtered into a gold basin. Sulphate and magnesium were precipitated with baryta; then barium and calcium were eliminated by repeated precipitation with ammonia and ammonium carbonate. The solution was finally taken to dryness in a platinum crucible, ammonium salts were volatilised and the mixed chlorides of potassium and sodium weighed as such. The potassium was then determined by the perchlorate /

TABLE 3.

Soil		Exchangeable Bases per 100 gm. air-dried soil.			
		CaO	MgO	K_2O	Na_2O
332	a.	·174	·013	·0186	·0082
	b.	·174	·010	·0173	·0073
337	a.	·387	·012	·0047	·0066
	b.	·383	·011	·0052	·0068

perchlorate method.

The perchlorate method of estimating potassium has received considerable attention from many analysts, and in view of the apparent lack of agreement on the subject, a series of preliminary experiments was carried through before deciding upon the best technique to employ. The results are given in appendix 2, p.77.

Except with soil 196, concordant results were obtained without the difficulty experienced by Hissink (loc. cit. p.146) in dealing with his humus sandy soils, and each figure in columns 6-10 of table 7 represents the mean obtained from duplicate experiments carried through with different samples of soil. The results in table 5 are quite typical.

The amounts of magnesium, potassium and sodium found in the second half litres never departed far from those obtained in blank experiments with the ammonium chloride solutions employed. For example the average weight of $Mg_2P_2O_7$ obtained from the second half litre from the first nine soils examined was ·0034 gm, more than 50 per cent. of the values lying between ·0026 and ·0042, and the $Mg_2P_2O_7$ obtained from 500 c.c. of the ammonium chloride solution was also ·0034. The average weight of NaCl + KCl obtained in the corresponding experiments was ·0130 gm, giving ·0035 gm. $KClO_4$, whilst a blank experiment gave ·0106 and ·0032 respectively. Those results seemed to offer fairly conclusive proof that the exchangeable magnesium /

magnesium, potassium and sodium were completely replaced by the first 500 c.c.* and that what was found in the second half litre constituted the impurities in the reagents employed and perhaps, as suggested by the figures for potassium and sodium, soil salts soluble in the aqueous solution. In one case (soil 196) a third half litre was collected and analysed for the alkalies. There was obtained .0132 gm. mixed chlorides giving .0026 gm. $KClO_4$ as against .0126 giving .0034 gm. $KClO_4$ and .0236 gm. giving .0147 gm. $KClO_4$ obtained from the second and first half litres respectively. Other samples of ammonium chloride used later gave much lower results (in one case as low as .0024 gm. NaCl+ KCl per 500 c.c. N. solution), but even the value .0130 might be regarded as a mere trace. However, in view of the very small quantities of exchangeable magnesium, potassium and sodium, those second half litre amounts were of considerable importance and were always deducted from the values for the first half litre before calculation.

Calcium was usually absent from the second 500 c.c. or present only in very small amounts. For example .004 per cent. was obtained in the case of soil 337, about 1 per cent of the total exchangeable calcium.

It was found that all the exchangeable calcium in soil 196 was obtained by leaching with 250 c.c. whilst in the case of soil 170, 250 c.c. extracted .265 per cent. CaO, a further .006 per cent. being obtained in the /

* Vandecavaye found that two extractions of a loam (Soil : Solution = 1:5) with $N.NH_4Cl$ replaced 90 per cent of Exchangeable potassium (105) Soil Sci.,1924,17, 91-96.

the second quarter litre. It appeared therefore that while 250 c.c. were insufficient to displace all the exchangeable calcium from a normal soil, 500 c.c.would besufficient. It is interesting to observe that the exchangeable calcium obtained from soil 170 by leaching with 500 c.c. N.NaCl amounted to ·273 per cent. CaO.

SOURCES of ERROR and PROBABLE MAGNITUDE.

In an investigation of this description it was essential to keep in mind the various sources of error and to obtain some idea of the extent of such error. In the first place there was the error involved in sampling the soil in the field and in the second place the laboratory error including the error involved in a second sampling and that incurred in the analytical procedure. It is convenient to consider the laboratory error first since data, upon which conclusions may be drawn, are available. Variations in the percentage of exchangeable calcium found in the first soil examined (196)led to the belief that the laboratory sampling error was very big* but that view was considerably modified on making a series of calcium determinations with soils 170 and 277. An air dried soil usually consists of finely divided material mixed with crumbs or larger particles which may conceivably be small stones. It was considered undesirable to grind the soil and hence sampling necessitated care in keeping the /

*Presumably the nature of the organic matter is the chief factor.

the proportions of fine material and larger particles as constant as possible. A fairly large sample of 170 was divided roughly into three parts. Part 1 was examined straightway for calcium but parts 2 and 3 were combined and the fine material separated from the coarser particles by means of a 1 mm. sieve. The calcium was determined in the two fractions obtained. The same was done with soil 277 and the results are collected in table 6.

Table 6.

Soil	Data	Part 1 Whole	Parts 2+3		Parts 2 3 together.
			< 1 mm.	> 1 mm.	
170	Weight % CaO	29.1 gm. .269	23.4 gm. .264	36.7 gm. .271	60.1 gm .268
277	Weight % CaO	28.1 gm. .213	34.2 gm. .204	23.1 gm. .226	57.3 gm. .213

It will be seen that in each case the finer material contained slightly less exchangeable calcium than the coarser particles probably due to the fact that the latter fraction consisted of aggregates, having binding material of great specific surface rather than small stones. Other soils might of course give a different result. The differences obtained are small but certainly much larger than experimental error as shown by a comparison of the figures in the third and sixth columns. Such concordance was not always obtained but throughout the investigation duplicate experiments with /

with only one or two exceptions gave results agreeing to within 1 per cent.

During the investigation thirty soils were examined by the same method giving thirty pairs of results for each base. Each pair of results has been taken, the mean calculated and the percentage deviation of each result from the mean. For calcium those percentages range from 0 to 1.7, exactly half lying between 0 and .4. From that it was considered justifiable to calculate the probable error of any mean by the least square method : $p.e. = \cdot 67\sqrt{\frac{\Sigma d^2}{n-1}}$ where d = deviation of each result from the mean and n = number of results. Thus for calcium $p.e. = \cdot 67\sqrt{\frac{15.2}{29}} = .37$. That is to say the probable error of any calcium result, introduced through laboratory sampling and analysis, is ·37 percent.

Treating the duplicate results for magnesium, potassium and sodium in the same way much greater percentage deviations were found as might have been expected from the very small quantities dealt with and the complicated analyses involved. The number of results did not seem to be numerous enough to justify the application of the method of least squares but at the same time there was no apparent reason for questioning the validity of the procedure. The probable errors were found to be 2.7 per cent for potassium, and 9 per cent for magnesium and sodium, all far in excess of the possible sampling error. The probable error calculated from /

from analyses of a number of solutions containing about the same amounts as the extracts examined, was only 1 per cent for all three bases. The discrepancy is probably due to two factors, namely the presence of large quantities of ammonium chloride and the minute quantities found in the second half litres.
Stewart (91), working with aqueous extracts of soils, found the percentage error in the determination of potassium to be about 4. His solutions contained only about one-tenth of the potassium contained in the extracts considered here, but he had not large quantities of ammonium chloride to deal with.

It is interesting to note how the error affects the relative proportions of exchangeable bases. Considering the results given in table 7 for soil 170, which is closely related to the average, a 10 per cent reduction in sodium scarcely affects the total and changes the relative proportions from 85.33 to 85.56 for calcium, 9.67 to 9.69 for magnesium, 2.24 to 2.25 for potassium and 2.77 to 2.51 for sodium.

The probable error in the pH determinations is negligible. A slight diffusion of potassium chloride from the calomel electrode may increase the hydrogen-ion concentration of the soil suspension, but by keeping the connecting arm out of the suspension except at the time of reading the E.M.F., the error is insignificant.

The error involved in determining soil moisture driven /

driven off at 105°C and the loss on ignition is almost entirely one of sampling.

The "Lime Requirement" values obtained by the Hutchinson and MacLennan method are not strictly comparable even when the conditions of the experiment are constant. The absorption of calcium depends upon the equilibrium concentration which will vary from soil to soil so that soils whose absorption of calcium is small will show a relatively greater "Lime Requirement" than soils with a larger absorption. Crowther and Martin (21) have evolved a method of extrapolation to a definite final concentration of bicarbonate from the results obtained in the usual way. The values given in table 7 have been recalculated according to that method but the differences found were small except with the most acid soils. Great stress is not laid upon the "Lime Requirement" figures but the results are submitted in appendix 3.

The field error due to variation in the soil presents great difficulty. Robinson and Lloyd (85) have dealt with the question as arising in soil surveys and from a critical examination of the results obtained in the analyses of a large number of borings, came to the conclusion that the field error was about 10 per cent for chemical analysis of total phosphate. It is questionable however if that result is applicable here and it would be idle to suggest the magnitude of the error until work has been done on the variation likely to /

Table III.7.

Exchangeable Bases in Soils

L.R.*	*p*H	M.†	L.I.‡	Soil	Milligram equivalents per 100 gm. air-dried soil						Percentage of total exchangeable bases (in Mg.E.)				
					Al+Fe	Ca	Mg	K	Na	Total	Al+Fe	Ca	Mg	K	Na
·196	5·45	5·49	6·74	417	·771	4·14	·694	·444	·610	6·66	11·58	62·16	10·42	6·67	9·16
·513	5·17	6·19	14·27	386	3·95	3·78	·744	·397	·390	9·26	42·66	40·83	8·04	4·29	4·21
·498	4·98	9·94	10·98	196	3·86	1·106	·347	·170	·119	5·60	68·90	19·73	6·20	3·03	2·13
·145	6·21	2·81	6·77	385	—	6·78	·298	·157	·187	7·42	—	91·35	4·01	2·12	2·52
·334	6·14	4·69	11·90	398	—	5·39	·744	·234	·187	6·56	—	82·19	11·35	3·56	2·85
·205	5·83	2·65	7·65	399	—	6·21	·744	·189	·297	7·44	—	83·41	10·00	2·54	3·99
·028	6·91	3·43	8·19	358	—	6·63	·149	·323	·355	7·46	—	88·94	2·00	4·33	4·76
·084	6·25	1·89	5·73	332	—	6·21	·595	·382	·252	7·44	—	83·43	8·00	5·14	3·38
·088	6·30	2·28	6·12	331	—	7·95	·893	·329	·236	9·41	—	84·55	9·49	3·49	2·50
·041	7·01	2·26	4·43	277	—	6·46	·446	·310	·329	7·54	—	85·59	5·92	4·11	4·36
·059	6·54	2·69	5·83	276	—	9·60	·794	·459	·316	11·16	—	86·00	7·11	4·11	2·83
·148	6·35	2·20	6·49	178	—	7·71	·794	·149	·361	9·01	—	85·55	8·81	1·65	4·01
·102	6·33	3·67	6·65	170	—	9·63	1·091	·253	·313	11·29	—	85·33	9·67	2·24	2·77
·067	6·11	4·43	5·81	169	—	10·42	·645	·123	·290	11·48	—	90·74	5·62	1·07	2·53
·096	6·16	2·41	5·36	355	—	10·21	·546	·187	·394	11·34	—	90·01	4·81	1·65	3·47
·041	6·94	3·25	9·03	337	—	13·74	·546	·106	·216	14·61	—	93·99	3·74	·73	1·48
nil	7·83	2·43	7·53	247	—	13·95	·546	·117	·142	14·76	—	94·73	3·71	·79	·96
nil	7·89	2·13	7·72	243	—	14·41	·347	·121	·136	15·01	—	95·98	2·31	·81	·90
·239	5·76	4·10	8·74	290	—	13·91	2·381	·353	·174	16·82	—	82·71	14·16	2·10	1·04
·188	6·09	3·91	12·69	343	—	19·90	1·637	·314	·384	22·24	—	89·50	7·36	1·41	1·73
				Average§	—	9·95	·776	·242	·269	11·24	—	87·88	6·95	2·46	2·71
													94·83		5·17

* L.R. = "Lime Requirement" as % $CaCO_3$.

† M. = moisture or loss at 105° C. per 100 gm. air-dried soil.

‡ L.I. = loss on ignition per 100 gm. air-dried soil.

§ Omitting Nos. 196, 386, 417.

likely to be found for exchangeable bases in a soil type. Each soil examined was a composite sample of from six to twelve borings taken at intervals over what appeared to be a uniform piece of ground.* The results submitted therefore can refer only to such a sample and that must be taken into account in discussing those results.

RESULTS.

The results are collected in table 7, the regularity of increase in total exchangeable bases being broken to keep together soils from the same locality. To simplify comparison of the quantities of different cations the results have been expressed in milligram equivalents rather than in percentages.

DISCUSSION OF RESULTS.

Since the number of comparable soils taken from any one locality is small, no attempt has been made to correlate pH and "Lime Requirement", but from the data given in Table 7 it will be seen that, in general, the most acid soils, as expressed by pH, have the greatest "Lime Requirements". While fair agreement is shown in the case of similar soils of the same origin, widely different soils provide several exceptions, as might be expected, since an acid condition may be the result of /

* In most cultivated soils the plough has formed a uniform surface layer by mixing different layers usually of the A horizon. The borings were always taken from the same group of layers.

of more than one factor. Jones (54), in an investigation of the pH and "Lime Requirement" of different soil types found no correlation between those values and Saint's (96) observations on soil acidity are essentially comfirmatory.

There has been a tendency in recent years to look upon the fertility of a soil as being dependent not so much upon its need for lime, as indicated by a figure for "Lime Requirement", as upon its content of exchangeable bases and in particular of calcium. For example great stress has been laid by Ssokolowski(90) upon the importance of the exchangeable calcium of a soil and Robinson and Williams (96) have demonstrated a close relationship between exchangeable calcium and response to liming. An unsaturated soil, according to modern views, is one in which hydrogen has replaced part or all of the exchangeable cations. A saturated soil on the same hypothesis is one in which the absorbing complex is completely saturated with bases. Hence there must be some relation between the degree of saturation and the reaction of a soil. As already pointed out (p.19) the degree of saturation (V) has been defined as the ratio of S, the quantity of absorbed bases actually present, to T, the total quantity which the soil is capable of binding. T, and therefore V, will obviously depend upon the content of absorbing material, organic and mineral, so that a low content /

TABLE 8.

Comparison of pH and Exchangeable Bases of a few Soils.

Soil	pH	Exchangeable Bases in milligram equivalents	
		Ca	Total
247	7.83	13.95	14.76
337	6.94	13.74	14.61
290	5.76	13.91	16.82
399	5.83	6.21	7.44
358	6.91	6.63	7.46

content of exchangeable bases (S) does not necessarily mean a low degree of saturation. Robinson and Williams have shown that a fairly close relationship may be found amongst similar soils between exchangeable calcium and pH, but the figures in table 8 combined with what has been stated above, show clearly that unless soils are similar in type little is to be gained from any generalisation in that direction.

Knowledge regarding S is very valuable but until a satisfactory method of determining V is devised, full advantage cannot be taken of it. A number of methods have been suggested. Hissink (47) obtained some comparative figures for V by assuming that T was approximately proportional to the percentage of particles less than ·02 mm in diameter. As he himself pointed out a considerable error may be introduced since two soils may be alike as regards content of particles less than ·02 mm, but quite unlike as regards content of particles less than ·002 mm. Furthermore, the presence of humus increased the uncertainty. The same worker (96) has attempted to determine T - S by estimating by a conductometric titration the amount of baryta required to saturate the soil. Only approximate results can be obtained however on account of the hydrolysis of the barium salt formed. Bradfield (9) got over that difficulty by titrating a base electrometrically with an acid clay suspension and there seems to be no reason why a modification of that method might not /

not be applied to a soil. Robinson and Williams (loc. cit) have suggested desaturating the soil completely with a dilute acid and carrying out an electrometric titration but it is not known if any such experiments have been carried out. If calcium carbonate is added to a soil before treating it with a neutral salt solution, the exchangeable hydrogen is more readily replaced owing to the side reaction between the hydrogen liberated and the carbonate. The carbon dioxide evolved might afford a means of measuring the degree of saturation and the practicability of the method has been commented upon by Page and Williams (96). Gedroiz (35a) has attempted to estimate the exchangeable hydrogen present in a soil, by replacing it by barium and titrating the extract with alkali but he admits that the method is not accurate. Probably the most satisfactory procedure that has been adopted is that of Bobko and Askinasi (7). They saturate the soil by leaching it with barium chloride and then replace the barium by means of ·05N hydrochloric acid. The barium in solution is then estimated. That gives a value for T, and S may be obtained by the usual methods of replacement. The absorbing complex is destroyed to a certain extent by the hydrochloric acid when a Tschernosiem or a permutite is so treated, but the absorbing capacity of a Podsol is not affected. Barium is not likely to be a constituent of many soil silicates so that any decomposition of the soil complexes should not /

not affect the result. Ramann (81/89) has stated that the absorption of ammonium hydroxide gives a guide to the degree of saturation of a soil but his evidence is not known and it seems likely that the experimental difficulties would be great owing to the volatile nature of the reagent and its deflocculating action.

At present the absorptive capacities of the soils examined are mot known but it is legitimate to compare the results obtained from soils of closely related types.

In the case of soils 169, 170, 178, 276, 355 there is a marked similarity in texture, origin and pH, and the fact that all five soils have an exchangeable base content approaching 11 milligram equivalents per 100 gm. soil probably indicates a like state of saturation throughout.

Soils 243 and 247 are almost identical in most respects. They come from the same area, have nearly the same pH and organic content and have no "Lime Requirement". Their contents of exchangeable bases are therefore quite comparable and we actually find a very close relationship. 331 and 332 also resemble each other in appearance and are very similar as regards pH, "Lime Requirement" and organic matter, but the total exchangeable bases and their relative proportions differ to an extent which might easily have been brought about by local conditions of cultivation and manuring. Such a probability will be discussed in the next section.

The /

The three soils containing exchangeable iron and aluminium are the most acid of the soils examined but there is so much difference in their contents of organic matter that it is not possible to draw conclusions. Attention, however, is directed to the fact that the area under cultivation (417) has a much smaller proportion of exchangeable tervalent bases than the adjacent uncultivated areas 196, 386. That is probably largely due to the lower content of organic matter in the cultivated soil. As Hissink (47) has indicated, the humus probably contains acids whose dissociation constants approach those of acetic or carbonic acids whilst the clay acids are reputably very weak. Those soils do not contain much clay so that their actual acidity must be governed largely by the organic acids and their "latent" or "exchange" acidity will depend upon the amount of humic acid present. The soluble iron and aluminium that are obtained by treating the soil with ammonium chloride solution may be the result of that exchange acidity. Of course on the other hand those bases may be present as exchangeable cations. That they are obtained only from the most acid soils may be due to the fact that those soils contain soluble iron and aluminium salts. The ready hydrolysis of those salts would account for the acid nature of the soils, but the question of their formation in absence of mineral acid seems to be an argument in favour of the former idea. A comparison of soils

398 and 343 however shows that the organic matter alone is not a determining factor. There is about 12 per cent of organic matter in each of those soils and the pH is 6.1 in both cases, yet the content of exchangeable bases and their relative proportions are widely different. Similar comparisons could be made with other soils but the results in table 8 are sufficient to demonstrate those fundamental differences due to soil type. All five soils contain about 8 per cent of organic matter so that the variation in pH and content of exchangeable bases is most likely due to variation in content of clay or its nature. The amount of the mineral absorbing complex, the sizes of its individual particles and its degree of saturation will all be important factors.

Until a sufficient number of soils have been fully examined and classified any generalisation is unwarranted but the results collected so far certainly give indications of what might be expected.

Soils of the same type or of similar types are probably very similar as regards absorptive capacity but there are almost certainly fluctuating differences due to cultivation and manuring to be taken into account. The physical condition of a soil is affected by the relative proportions of the absorbed bases but changes in that direction are likely to be too small to alter the type except in abnormal cases. The exchangeable hydrogen also disturbs the colloidal-chemical /

chemical equilibrium and will eventually change the type as determined by colour, texture and drainage. It will also be largely responsible for the soil reaction except when there are large amounts of exchangeable univalent cations*. Soils of different types may be extremely dissimilar as regards absorptive capacity due to the nature and amount of the absorbing complex.

Hence the content of exchangeable bases in a soil and its reaction are likely to prove characteristic of a soil type.

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*A sodium complex is very unstable and may impart a fairly alkaline reaction to a soil although it is not completely saturated.

THE RELATIVE PROPORTIONS OF EXCHANGEABLE BASES.

Reference has been made on more than one occasion to the relative proportions of the exchangeable bases present in a soil, and many workers have dealt with the importance of the question. Gedroiz (29-36) has indicated how the structure of the soil is influenced by the nature of the colloidal complexes and how the composition and nature of the complexes may be altered under the influence of fertilisers. He was able to demonstrate the changes which could occur by saturating a soil with various bases differing in valency and atomic weight. He came to the conclusion that the predominating factor was the chemical composition of the complex, its degree of dispersion being directly correlated with the valency and atomic weight of the cation. He also submitted an explanation of the presence of sodium carbonate in "alkali" soils and a suggestion for the best corrective treatment(32).

Soils in which the bivalent cations predominate have come to be regarded as normal soils and Hissink(47) has discussed at length the effect of sea flooding upon such soils. He has shown how the content of exchangeable sodium is greatly increased at the expense of the calcium and how both the organic and mineral parts of the absorbing complex are so influenced as to produce a remarkable deterioration in the soil structure. A porous structure may be preserved as long as there are soluble /

soluble salts present to exert a flocculating action, but when they are washed out deflocculation takes place. Calcium carbonate is most important in the treatment of those "sodium soils". It goes into solution as bicarbonate which not only flocculates the complexes but brings about replacement of sodium by calcium. He has also given figures to show how manuring (with and without lime) has altered the content of exchangeable bases and their relative proportions in a number of clay soils.

The alkali soils in America have also been examined (56-58) and the views expressed by the workers there are quite in harmony with those of Gedroiz and Hissink. Kelley and Brown(57) comment upon the differences found in the proportions of exchangeable bases of normal soils and suggest that the age of the geological formation may be a factor.

In this country Page and Williams (96) have dealt with the relationship between manuring and the amounts of exchangeable bases in a particular soil. They have shown that constant manurial treatment may alter the total and relative proportions of exchangeable bases to a considerable extent even in presence of excess of calcium carbonate.

At the same time it is interesting to note that Niklas and Vogel (68), from an examination of 2000 Bavarian soils, concluded that as far as soil reaction was concerned the determining factor was the parent material /

Table ₹9. *Results obtained by other investigators*.*

Investigators and soils examined		Exchangeable bases				
		Total in Mg.E.	Relative proportions			
			Ca	Mg	K	Na
Gedroiz	Tshernoziem	55·0	82	15·5	2·7	nil
	Podsol	6·25	80	13·5	6·4	nil
Hissink	Average of 26 clay soils	38·3	79	13	2	6
	Average of 7 clay soils without $CaCO_3$ and soluble salts	35·4	84·2	11·3	1·4	3·1
	Average of 2 sandy humus soils ...	19·8	76·3	13·1	3·0	7·6
Page and Williams: Surface soil unmanured plot		14·74	92·1	5·1	2·8	nil
Kelley and Brown	Average of 7 neutral or slightly alkaline soils ...	30·3	63	25	4	8
	Average of 6 acid soils ...	6·6	—	—	—	—†
Smith: Average of 17 Scottish soils		11·24	87·9	6·9	2·5	2·7

* Alkali soils have not been included.

† Tervalent bases are present in varying amounts and the results here are too variable to justify the giving of an average.

material of the soil and so-called acid fertilisers were only of secondary importance.

Table 9 has been submitted to indicate the interesting differences to be found in soils of different countries. A critical comparison cannot be attempted but it is noteworthy that except in the case of alkali soils and soils having exchangeable tervalent bases, calcium is invariably the predominant cation whether the soils are heavy clays or are of a humus-sandy nature.

A considerable amount of data on soils in their natural condition is therefore available but it seems that no work has been done in the laboratory on the effects which may be produced by limited quantities of neutral salts. It was thought that interesting results might be obtained by treating different soils with dilute solutions of different salts and measuring the changes in the proportions of exchangeable bases. The experiments to be described were designed to throw light principally upon the effect of the same manurial treatment on different soil types.

EXPERIMENTAL.

The Soils Examined.

Five soil types were employed in this part of the investigation and the soils examined were 170, 277, 290, 331, and 337. They have been described on pages 33-38 and were all sampled between September 1924 /

1924 and March 1925. Soil 170 was again sampled in September 1925 and has been called 170 N.

The Solutions Employed.

Soils 331 and 170 N were treated with a solution containing potassium chloride and sodium chloride in equi-molecular amounts and $\frac{N}{50}$ with regard to chlorine. 170 N was also treated with that solution diluted 10 times. Soils 170, 277, 290, 337 were treated with $\frac{N}{50}$ calcium chloride solution and 277 was also treated with that solution diluted 10 times.

Methods.

In each experiment the soil and solution in the ratio of 3 gm. to 10 c.c. were shaken at room temperature for about an hour and allowed to settle. Except when $\frac{N}{500}$ solutions were employed the supernatant liquid became quite clear. With the $\frac{N}{500}$ solutions the supernatant liquid remained quite turbid below the top $\frac{1}{2}$ inch or so, even after several days, and the subsequent filtration was very slow. That was doubtless due to insufficient electrolyte being present to bring about flocculation, because when 277 was shaken up with distilled water the supernatant liquid was quite turbid except for the top $\frac{1}{2}$ inch, even after standing for a fortnight. The flocculation would of course depend upon all the ions present in the solution so that replaced ions would play a part. In

other /

other words replaced calcium would increase the flocculating power of an alkali chloride solution whilst replaced univalent ions would decrease the flocculating power of a calcium chloride solution. Furthermore the relative amounts of exchangeable bases in the soil complex would affect the degree of dispersion but even when $\frac{N}{50}$ alkali salts were employed the increase in the percentage of univalent cations was insufficient to produce a stable suspension because calcium would be liberated in sufficient amount to bring about flocculation.

The supernatant liquid was filtered through a Buchner funnel and refiltered to get a perfectly clear solution. The soil was then transferred to the paper and washed with distilled water. In experiment 2 it was then dialysed for several days in a parchmont bag until only a trace of chlorine could be detected in the outside water. In the other experiments it was found that continued washing on the filter was quite efficient. The soil, free from all but minute traces of salts, was then transferred to a basin and dried at room temperature. About 150 gm. of soilwere taken for each experiment and about 99 per cent. was recovered. The loss, which was due partly to the difficulty experienced in removing the fine material completely from the filter paper, is reflected in the decrease in total exchangeable bases and loss on ignition (table 10). The air dried soil was examined for exchangeable bases as described in the last section and measurements of pH /

TABLE 10

Expt.	Treatment.	Soil	% Loss at 105°C	% Loss on Ignition	Exchangeable Bases: Total (Mg.E.) percent.	Exchangeable Bases: Percentage of Total: Ca	Mg	K	Na	pH.	Changes in Solution: pH: Before	After	Mg.E. in 1000/3 c.c. solution: Cations: Before	After	Chlorine: Before	After
1		331	2·28	6·12	9·41	84·55	9·49	3·49	2·50	6·30						
1a	KCl + NaCl (N/50)	331a	2·10	5·66	9·10	69·79	9·45	18·68	2·09	6·99			6·71	7·06	6·78	6·93
2		170N	2·94	7·01	10·83	88·43	8·70	1·34	1·53	6·10						
2a	KCl + NaCl (N/50)	170Na	2·22	6·72	10·67	76·23	7·12	14·28	2·38	6·35	6·21	5·71	6·75	6·97	6·79	6·87
2b	" " (N/500)	170Nb	2·42	6·56	10·73	88·84	7·41	3·23	·54	5·95						
2c		9/10 170N + 1/10 170Na	—	—	11·32	85·65	8·47	2·92	2·94	6·23						
2d		2c calc.	—	—	10·81	87·21	8·55	2·64	1·61	—						
3		170	3·67	6·65	11·29	85·33	9·67	2·24	2·77	6·33						
3a	N/50 $CaCl_2$	170a	2·46	5·79	10·83	96·23	1·42	1·31	1·07	6·85			6·91	7·17	6·83	6·93
4		337	3·25	9·03	14·61	93·99	3·74	·73	1·48	6·94						
4a	N/50 $CaCl_2$	337a	2·67	8·27	15·38	96·58	1·89	·81	·73	7·94?	6·21	—	6·76	6·08	6·75	6·81
5		290	4·10	8·74	16·82	82·71	14·16	2·10	1·04	5·76						
5a	N/50 $CaCl_2$	290a	3·79	9·34	18·80	83·16	14·79	1·33	·72	7·56?	6·21	—	6·76	7·02	6·75	6·86
6		277	1·81	4·35	9·01	84·29	9·15	3·69	2·89	6·98						
6a	N/50 $CaCl_2$	277a	1·27	4·16	8·28	91·49	4·80	2·90	·81	6·81	6·17	6·47	6·76	6·89	6·75	6·81
6b	N/500 "	277b	1·38	4·70	8·42	87·64	7·93	2·89	1·56	6·63	6·59	6·76				
6c		9/10 277 + 1/10 277a	—	—	8·87	85·39	7·85	3·60	3·17	6·94						
6d		2c calc.	—	—	8·94	85·01	8·71	3·61	2·65	—						
	Before storing	277	2·26	4·43	7·54	85·59	5·92	4·11	4·36	7·01						
7	Sampled 1924	178	2·20	6·49	9·01	85·55	8·81	1·65	4·01	6·35						
7a	" 1925	178 N	2·56	6·07	7·40	92·06	4·06	1·85	2·03	—						

pH, moisture and loss on ignition were also made.

The solutions were completely analysed before and after contact with the soil and the results have been calculated to express the milligram equivalents (Mg.E.) present in 1000/3 c.c. which was the volume of solution used for each 100 gm. of soil.

All the results have been compressed into table 10 in order to facilitate comparison. The soil examined in experiment 2c was obtained by mixing 9 parts of the original soil 170 N with 1 part of the soil obtained by treating 170N with the $\frac{N}{50}$ solution: similarly in case 6c; 2d and 6d are simply the results calculated from 2 and 2a and from 6 and 6a respectively The pH values for 4a and 5a are doubtful owing to the probable contamination of the soils with ammonia fumes.

DISCUSSION of RESULTS.

Changes in Soil

The outstanding feature of the results is the great influence exerted by $\frac{N}{50}$ solutions except in experiment 5 which will be commented uponlater.

Effect of $\frac{N}{50}$ Alkali Chlorides. The alterations in soils 331 and 170N effected by $\frac{N}{50}$ (KCl + NaCl) were much greater than anticipated. Both soils were sticky after the treatment and difficult to dry; the reason for that becomes evident when the exchangeable bases are considered. There is a remarkable increase in exchangeable /

exchangeable potassium chiefly at the expense of calcium. The sodium which might have been expected to bear a close relationship to the potassium, has scarcely been affected. There is an apparent slight decrease of sodium in 331a and a small increase in 170 Na. That potassium has a greater energy of absorption than sodium has been revealed by the observations of many workers. For example Lemberg's experiments on leucite and analcite (61) showed that potassium was a much more active replacing agent than sodium under similar conditions. Then it is interesting to note that Hopkins, Knox and Petit (52) in quite a different manner demonstrated the same thing. They based their method of determining the "Lime Requirement" of a soil on the absorption of the base from a neutral salt. The replacement was not complete and for routine analyses they recommended a factor 3 when sodium chloride was employed. That factor was reduced to 2½ when a potassium salt was used. Daikuhara(23) also showed that sodium gave lower results than potassium and recommended the factors 3·5 and 3. The details of the methods are unnecessary to indicate that those workers were aware that potassium replaced cations more vigorously than sodium. Hissink(47) showed that potassium chloride displaced calcium from a soil more quickly than did sodium and other workers* have drawn up a series of cations in their order of replacing power. However the cations already present in the absorbing /

*See Kelley and Cummins(56) and Ramann(81)

absorbing complex influence the absorption and as Gedroiz[34], and more recently Wiegner[104], have pointed out, a true indication of the energies of absorption of cations can be obtained only by examining their absorption by a complex saturated with one other cation. Those last mentioned investigators have concluded that the degree of hydration of a cation and its valency are directly related to its energy of absorption which is thus closely connected with its flocculating power. The series of univalent ions Li, Na, NH_4, K, Rb, Cs, shows increase in atomic weight and decrease in degree of hydration in that order and equimolecular solutions show increasing powers of flocculation and cation replacement in the same order. Gedroiz carried out experiments with soils saturated with one cation whilst Wiegner worked with clays. The present case is complicated by the fact that a mixture of chlorides was used but the salts were present in equimolecular amounts and there has obviously been a selective absorption of the cations.

Effect of $\frac{N}{50}$ $CaCl_2$. The changes brought about by the calcium chloride do not seem to be so pronounced as those effected by the alkali chlorides, but that is because calcium is the predominating base to begin with. Generally speaking the content of exchangeable calcium has increased at the expense of the other three /

three cations. It is not legitimate to compare the relative effects of calcium and potassium as displacing agents, for reasons already mentioned, but it would appear that magnesium is replaced more easily by calcium than by potassium and sodium. Gedroiz showed that such was undoubtedly the case with a soil saturated with magnesium but Wiegner has stated (loc. cit. p.366) that potassium replaces calcium more vigorously than calcium replaces potassium, and the two points are difficult to reconcile.

Effects of Manurial Treatment. It was realised that those quantities of salts were far in excess of what might be employed in the field. The ratio 10 : 3 for solution to soil corresponds to 30" rainfall held up in the top 7"-8" soil, (assuming that an acre of soil to that depth weighs about 2,000,000 lbs) but the ratio of salt to solution ($\frac{N}{50}$) is ten times as great as a dressing of 10 cwts of mixed alkali chlorides per acre. Two methods were adopted to arrive at some idea of the change which might be expected to take place in actual practice.

(A) To increase 10 times the amount of soil taken was impracticable but it was thought that, in view of what has been said on p.29, there might exist some rough proportionality between the absorption and the quantity of soil employed. Accordingly experiments 2c and 6c were carried out (see p. 63) and the calculated /

calculated results 2d and 6d are added for reference. It will be observed that there is a fairly close agreement between c and d in spite of the different equilibria which must have been set up and the increase in probable error involved in such a calculation.

(B) In this case the solution was diluted 10 times giving results 2b and 6b. A greater change in the original soils is obtained than that calculated for a tenfold increase of soil with $\frac{N}{50}$ solution (d). That was expected since in the first place the absorption does not increase quite so rapidly as the amount of absorbent (d will give a low result) and in the second place the absorption is not quite proportional to the solution concentration (a. will not give as much as 10 times the absorption found in b.) The treatment in B is analogous to the effect of 1 cwt. of salts per acre and 3" rain on the top $\frac{3}{4}$" layer of soil or to 10 cwts., 30", and 7"-8" respectively. Whether B gives a close approximation to what might occur is open to question, but that the alteration found by A and B is of the same order as that due to manurial treatment in the field, is evident from the results quoted by Hissink and Page.

Those changes are small and show that ordinary manurial treatment is not likely to alter the soil type unless in reaction. They are more in the nature of fluctuating differences and it is quite likely that

they /

they are not greater than field error. There will be secular changes due to weathering, which really amounts to replacement of bases by hydrogen and gradual decomposition of the complexes, and there will be seasonal changes for there is almost certain to be a relationship between the exchangeable cations and the soil solution. Now there is a decrease in the concentration of the soil solution on cropping, with a recovery before the next season (91,14) and moreover that concentration may increase on storing a soil and even more so on fallowing(14). Soil 277 was analysed shortly after sampling in January 1925 and the results are contained in table 7. It was again analysed in November 1925 and the results are given in table 10. There is quite a big difference, particularly in magnesium, and it cannot be accounted for except by assuming that the storing effected an increase in the amount of exchangeable bases. Except for 277 and 170 N the soils in table 10 were not analysed immediately before treatment so that the alterations found may not have been due entirely to the salts added. Soils 170 and 178 were sampled in September 1924. They were sampled again twelve months later - 170N and 178N. In the interval a crop of oats (no "artificials" added) had been taken from 170, and cattle and sheep had been grazed on 178 (grass after barley). The changes are more likely to be due to field error than to cropping and an illustration of the variation which is to be expected in any soil type.

CHANGES /

CHANGES in SOLUTION.

It is generally agreed that base exchange does not alter the concentration of the solution provided secondary reactions do not take place, but the acidity of the soil and of the solution must be considered. If the solution is more acid than the soil then hydrogen also will replace cations and increase the base content of the solution; the converse will also hold. Table 10 includes the pH values for most of the experiments. Except in experiment 4 the concentrations of the solutions were increased by contact with the soil. The differences are probably not much greater than experimental error and the loss of organic matter has no doubt affected the acidities of the soils, but the fact that in experiment 6 alone the result agrees with the hypothesis put forward to explain cation exchange, seems to indicate that solubility effects have influenced the other results. Kelley and Brown (57) have attributed the discrepancy between ammonium absorbed and cations replaced to such an influence.

The invariable "negative absorption" of chlorine is most interesting. It is improbable that it is due to soil salts since the solutions were $\frac{N}{50}$ with respect to chlorine, and an experiment with soil 277 showed that it was not due to concentration by filtering under reduced pressure. It is noteworthy that Cushman's results (22) show an absorption of chlorine by clay from $\frac{N}{10}$... ammonium chloride, and chlorine may be /

be removed from hydrochloric acid by soils[80]. Clay particles possess a negative charge throughout a range of pH 2.1 - 12.7[51] and it has been shown by the writer that in presence of organic matter the charge on a soil particle is negative (see appendix 4) The heterogeneous character of the soil system has prompted investigators to seek an explanation of the behaviour of the soil complex in the well known electrical double layer theories of Helmholtz, Hardy and others. There will be ionisation of the surface molecules which will leave the ultramicron negatively charged. Addition of acid will reduce the ionisation and may ultimately reverse the charge and so permit anion absorption[38]. That of course is unlikely to occur to a soil without radical changes being affected in its constitution. On the other hand addition of alkali will lead to increased dissociation with an increase in the negative charge and that appears to be the explanation offered by Mattson[66] for adsorption of calcium hydroxide. Other soil phenomena have been explained in a similar manner on the basis of a Donnan equilibrium as developed by Loeb[63] in his work on proteins (see 95 and Comber 96). It is easy to visualise an ultramicron surrounded by cations whose number is determined by the nature of the ultramicron but whose composition may be varied by the addition of electrolytes. The electric potential between the ultramicron and the cations will depend upon the

nature /

nature of the cations. Sodium for example is univalent and considerably hydrated so that a sodium complex will be very stable and hydrophilic in character. Calcium on the other hand will be much more effective in reducing the charge and a calcium complex will be comparatively unstable. Wiegner(104) has developed that idea to explain the flocculation of different clays and has shown how base exchange may play a big part in disperse systems and how the properties of the disperse phase may be largely determined by the hydration of the absorbed ion. Wheeting(102) showed the same thing from "heat of wetting" and freezing point measurements on colloids. As Hissink has pointed out there may be particles of molecular dimensions in an aqueous soil suspension (particularly in the organic part) and the exchange process will then become a chemical reaction, but by regarding the complex as an insoluble colloidal acid associated with hydrogen and bases at the surface, Page(72a) has been able to show that nearly all the properties of the soil can be brought into line by a simple chemical explanation.

Enough has been said to indicate the physico-chemical importance of exchangeable bases and their importance in the physiological processes may be briefly dealt with. No satisfactory method of analysis has been developed to supply criteria of soil productivity(55,65) because the soil is so complex that it /

it is impossible to select a solvent capable of differentiating between substances available and non-available to the plant. As a matter of fact the question as to what is meant by the available state is still unanswered. Substances in true solution are available but the complex processes of nutrient assimilation by the roots are little understood. There will be osmosis influenced by the nature of the solution and the character of the cell membrane. Christensen [17] inter alia has emphasised the importance of a physiologically-balanced solution and Truog[98] has adduced evidence to show that the cell sap itself probably plays a part. Although Comber[19] has suggested that union of the root hairs with soil particles to form a single system may permit of direct absorption of colloids, most attention has been directed to the availability of the absorbed bases. That they are indirectly available as a result of weathering and addition of fertilisers is undisputed but whether a plant can absorb them without solution changes and whether bases which are not in exchangeable form can be assimilated are problems still unsolved. There is evidence that absorbed potassium may be made available by the action of water[39,88] and that a plant is nourished only by substances in solution or absorbed[59], but the general conclusion arrived at from different investigations with permutite is that the exchangeable cations are not available unless soluble salts are present. Nostitz[69] has /

has suggested that a small part of the complex may be easily degraded by separation of the bases so that unless a supply of replaceable ions is maintained that part may be broken up and the absorptive power of the soil decreased. Hissink is inclined to believe that there is no reciprocal action between the bases in exchangeable form and those soluble only in acids unless there are surface changes, and that the former are by far the more important in plant assimilation. Hence a knowledge of the exchangeable cations of a soil is most desirable. The information concerns a fundamental property and is far more valuable than the results obtained by the many arbitrary methods of soil analysis. Acid extractions for example cannot do more than give a rough idea of a soil's sources of reserve material. Unfortunately, however, the determination of the exchangeable cations is a most tedious and time-consuming procedure and as carried out at present cannot be recommended for routine soil analysis. It is difficult to foresee how the method can be simplified but there are indications that when different soil types have been fully examined it may be curtailed to suit a soil belonging to one of those types. It is also possible that there may be some relation between the total content of exchangeable bases and the fraction which can be extracted by CO_2- water in any type.

C O N C L U S I O N S.

The following conclusions may be drawn from the results obtained in this investigation and the extensive literature on the subject:- The content of exchangeable bases is determined by the amount and condition of the absorbing complex, and the amount of the complex and its condition are characteristic of soil type. The condition of the complex will depend largely upon the composition of the absorbed cations, but under ordinary circumstances the relative proportions of those cations are not likely to undergo sufficient alteration to produce rapid changes in the condition of the complex. The changes which are effected in a few years are probably not greater than the variation occurring in any soil and, as has been suggested there may be changes brought about by storing. At the same time there are much bigger differences which are certainly fundamental soil differences. Those will be due not only to the amount of the absorbing complex but also to its nature. It may be largely mineral or it may contain a considerable amount of organic matter and moreover its degree of dispersion will affect its "activity" as an absorbent. Hence although absorptive power and its relation to fertility may not be a convenient method of soil classification (as suggested by /

by Way) it is extremely likely that soil types distinguished in the field will be found to possess characteristic absorptive properties. Perhaps the importance of the exchangeable bases has been over-estimated but in the light of present knowledge and the very satisfactory working hypothesis on the subject, there is reason to expect that base exchange will continue to occupy increasing attention.

TABLE 11.

COLOUR OF EXTRACT AND ORGANIC MATTER.

Soil No.	Colour of Extract.	Per cent loss on ignition	pH	Exchangeable Bases	
				Total per cent	Per cent univalent
277	a.c.	4.43	7.01	7.54	8.5
355	a.c.	5.36	6.16	11.34	5.1
332	c.	5.73	6.25	7.44	8.5
169	c.	5.81	6.11	11.48	3.6
276	p.g.	5.83	6.54	11.16	6.9
331	c.	6.12	6.30	9.41	6.0
178	p.g.	6.49	6.35	9.01	5.7
170	c.	6.65	6.33	11.29	5.0
* 417	a.c.	6.74	5.45	6.66	15.8
385	c.	6.77	6.21	7.42	4.6
247	p.g.	7.53	7.83	14.76	1.8
399	p.g.	7.65	5.83	7.44	6.5
243	p.g.	7.72	7.89	15.01	1.7
358	p.g.	8.19	6.91	7.46	9.1
290	a.c.	8.74	5.76	16.82	3.1
337	c.	9.03	6.94	14.61	2.2
* 196	g.	10.98	4.98	5.60	5.1
398	a.c.	11.90	6.14	6.56	6.4
343	p.g.	12.69	6.09	22.24	3.1
* 386	p.g.	14.27	5.17	9.26	8.5

c. = colourless; a.c. = almost colourless;
p.g. = pale green; g. = green.

* contain Fe, Al.

APPENDIX I.

In many cases the first portion of the ammonium chloride extract was coloured green due no doubt to the ammonium complex of part of the organic matter forming a true or colloidal solution. The possibility of that material preventing the precipitation of iron and aluminium was not overlooked and table 11 was compiled to discover if there was any relationship to be found among such values as are collected there. There is no apparent correlation between content of organic matter and colour of the first half litre extract so that the condition of the humus was probably of greater importance. Iron and aluminium were obtained only from the most acid soils and if the organic matter did play a part in preventing the precipitation of those bases in other cases, then it seems safe to say that they were present only in very small quantities. Of course the Comber test indicates that iron is invariably present in acid soils but the amount required to produce a colour with thiocyanate is minute. The pH values of soils 399 and 290 suggest that iron and aluminium might have been present, although they were not precipitated.

APPENDIX II /

APPENDIX II.

ESTIMATION of POTASSIUM.

According to investigations on the perchlorate method of estimating potassium, there are three main sources of inaccurate results(24,67,72).

(a) The perchloric acid may contain considerable amounts of chloric acid and too low a concentration of perchloric acid to decompose the chlorates and chlorides.

(b) The presence of sulphate gives rise to difficulties particularly in the Nebauer method which involves the addition of calcium carbonate.

(c) The washing of the precipitate to dissolve the sodium perchlorate demands careful attention in view of the not-insoluble nature of the potassium salt.

The following experiments were carried out to decide upon the most satisfactory technique for the determination of the exchangeable alkalies.

The acid employed was B.D.H. 20 per cent. 10 c.c. gave a residue of ·0028 gm. on evaporation, but that was quite soluble in 97 per cent alcohol. 2 c.c. of the acid always proved to be sufficient to give off copious fumes at the end of the evaporation with the mixed chlorides.

A solution (A) was prepared containing ·6323 gm. pure potassium chloride in 500 c.c. water. 10 c.c. of that solution therefore contained ·01265 gm., which was comparable to the amounts of potassium obtained in /

in the soil extracts. A solution (B) containing ·6323 gm. pure potassium chloride and ·4696 gm. pure sodium chloride in 500 c.c. was also prepared. In each solution 10 c.c. was equivalent to ·0235 gm. $KClO_4$.

In each determination 10 c.c. were taken to dryness with about 2 c.c. perchloric acid in a glass basin and the residue was allowed to cool. Then about 8 c.c. of a solution containing 98 per cent alcohol and ·4 per cent perchloric acid were added and the whole was triturated and set aside for 30 minutes. The supernatant liquid was was then decanted into a Gooch filter. In experiments 1, 2, 3, the residue was then brought into the crucible and washed with the alcoholic solution. In experiment 4 a few drops of perchloric acid were added to the residue. The contents of the basin were then taken to dryness and treated as in the first three cases. In experiment 5 there was a second washing by decantation before introducing the precipitate into the filter. The means of duplicate results are given in table 12.

Table 12.

Solution.	Expt.	gm. $KClO_4$	Filtrate c.c.
A	1	.0235	35
A	2	.0237	18
B	3	.0244	14
B	4	.0231	25
B	5	.0238	25

In every case the Gooch crucible was dried at 130°C to 140°C for 20 minutes. The method decided upon /

upon as being the most suitable was that adopted in experiment 5:- two decantations followed by washing to make the total filtrate 15-25 c.c. depending upon the weight of mixed chlorides dealt with.

The following experiments carried out with extracts from soil 196 were instructive as showing how the presence of sulphate might vitiate the results. A. refers to the first 500 c.c. and B. and C. to the second and third respectively.

In experiments 3 SO_4'' was not removed before weighing the mixed chlorides, and its presence was detected in the perchlorate. In experiment 4A the mixed chlorides were weighed than taken up with water and a little baryta and filtered. After removing excess barium by repeated precipitation with ammonia and ammonium carbonate, and getting rid of the ammonium salts, the mixed chlorides were again weighed 4A'. In 4B sulphate was precipitated before removing the calcium from the extract and the same procedure was adopted in experiment 6. See table 13 for results.

Table 13.

Expt.	gm.(KCl + NaCl)	gm. $KClO_4$
3A.	.0290	.0204
3B	.0158	.0052
4A	.0259	-
4A'	.0218	.0153
4B	.0124	.0035
6A	.0236	.0147
6B	.0126	.0034
6C	.0132	.0026

The probable error in those determinations has already been discussed.

APPENDIX III /

TABLE 14.

LIME REQUIREMENTS.

Soil	y	$\frac{A}{\log x}$	L.R. for B′	L.R. for B″	Ordinary L.R.
386	7.06	.1529	.494	.567	.513
196	7.15	.1474	.477	.547	.498
398	8.10	.0932	.301	.346	.334
290	8.65	.0647	.209	.240	.239
399	8.85	.0548	.177	.203	.205
417	8.90	.0523	.169	.194	.196
343	8.95	.0499	.161	.185	.188
385	9.20	.0379	.123	.141	.145
178	-	-	-	-	.159 ?
170	9.45	.0263	.085	.098	.102
355	9.48	.0249	.081	.092	.096
331	9.53	.0226	.073	.084	.088
332	9.55	.0217	.070	.081	.084
169	9.65	.0172	.056	.064	.067
276	9.70	.0149	.048	.055	.059
277	9.80	.0105	.034	.039	.041
337	9.80	.0105	.034	.039	.041
358	9.88	.0069	.022	.026	.028
247	10.08	0	-		Nil
243	10.05	0	-		Nil

APPENDIX III.

"LIME REQUIREMENTS"

It has been pointed out that the "Lime Requirement" as determined by the Hutchinson and MacLennan method depends upon the conditions of the experiment and the final concentration of bicarbonate in solution.

The final concentration depends upon the initial concentration and the soil in question. All the determinations were made with the same bicarbonate solution at the same time. 20 gm. soil and 300 c.c. solution were placed in a bottle: the air was displaced by carbondioxide: the bottle was shaken for 3 hours and its contents filtered: 100 c.c. of the filtrate were titrated with .2295 N. hydrochloric acid. 100 c.c. of the original bicarbonate solution were equivalent to 10.04 c.c. acid.

Expressing all concentrations in the form c.c. $\frac{N}{10}$ in 300 c.c., and putting A = initial concentration, B = final concentration, W = weight of soil required to effect reduction A - B, then "Lime Requirement" (L.R.) = $(A-B) \times {}^{.5}/_{W}$ per cent. $CaCO_3$ -(1).

If 20 gm. soil reduce the concentration of bicarbonate from A to X then

$$\frac{1}{W} \log\frac{A}{B} = \frac{1}{20} \log\frac{A}{X}^{*}$$

$$\text{Hence L.R.} = (A-B) \times .025 \times \left\{\log\frac{A}{X} \quad \log\frac{A}{B}\right\} = 2.$$

Let /

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* Crowther and Martin[21] have shown that for any one initial concentration, W plotted against log B gives a straight line, i.e. $\frac{1}{W} \log {}^{A}/_{B} = K.$

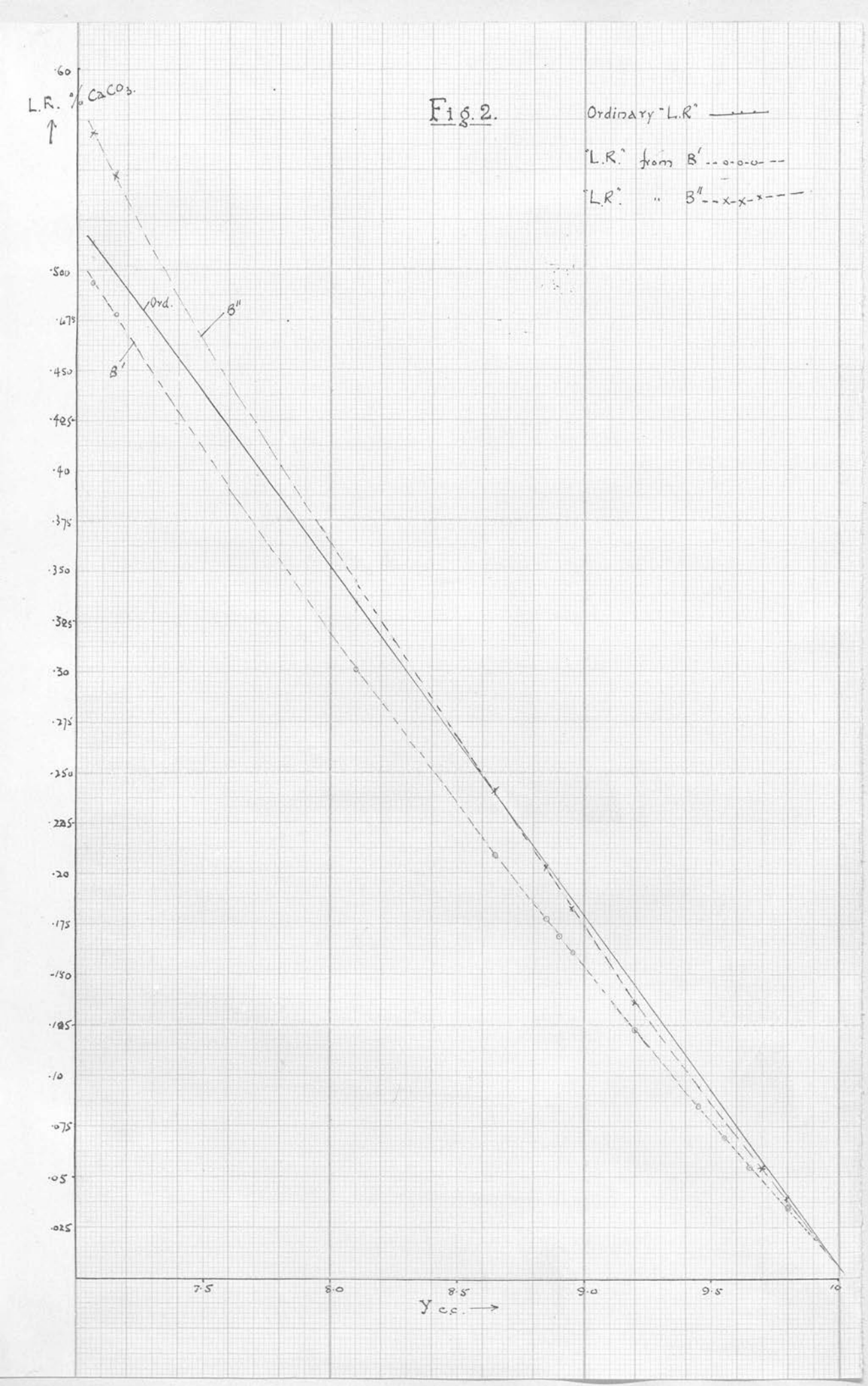

Fig. 2.

Ordinary "L.R." ——·——·——

"L.R." from B' - - o - o - o - -

"L.R." " B'' - - x - x - x - - -

Let the final concentrations be B' (.015N) and B" (.020 N)

Then A = 10.04 × 3 × 2.295

B' = 45, B" = 60

x = y × 3 × 2.295 where y = c.c. acid required for 100 c.c. filtrate

$$\log \frac{A}{x} = \log \frac{10.04}{y}$$

Hence L.R. = $24.11 \times \frac{.025}{.186} \times \log \frac{10.04}{y}$ for B'

= $9.11 \times \frac{.025}{.0614} \times \log \frac{10.04}{y}$ for B"

The results have been calculated for those two final concentrations and are collected in table 14. See Fig. 2.

If y is plotted against L.R. calculated in the ordinary manner a straight line is obtained, because L.R. = (A-y) × 5× ·005 = ·025 (A-y). In equation 2 however the L.R. is proportional to $\log \frac{A}{y}$. If X (the actual final concentration) is equal to B, then equations 1 and 2 are identical. That occurs in the case of L.R. for soil 290, but of course X will usually be unequal to the selected B. When X is greater than B then the calculated L.R. is less than the ordinary L.R., and it will be observed that such is always the case here when B is .015N. That indicates that even with the most acid soils the concentration is never reduced to .015N. When X is less than B then the calculated L.R. is greater than the ordinary L.R. Obviously the closer B approaches A the more frequently that will occur. When B. is .02N three /

three soils are so involved showing that they have reduced the initial concentration to below .02N. As mentioned above 290 has reduced the concentration to a value close to .02N. An intersection of the curves for ordinary L.R. and L.R. calculated to B" (.02N) is therefore found. The differences are very small and scarcely important in view of the fact that concentration is not the only factor which affects the absorption. The energy of absorption of the various ions in solution will play an important part at the dilutions employed.

APPENDIX IV. /

APPENDIX IV.

CHARGE on the PARTICLE.

An attempt was made to wash soils 417,337,243, 247,290,343, which had been leached with ammonium chloride. After two decantations with distilled water the supernatant liquid became deeply coloured. It was slightly opalescent but quite transparent and there was scattering of light. The liquids were dialysed for 18 hours and although chlorine was detected in the outside water there was no diffusion of the colour, indicating that the washing had not been complete and that the colour was due to substances in colloidal solution or at least of large molecular dimensions. The colour changed from yellowish brown to dark reddish brown in the order 417,337,243,247, 290,343, which, incidentally, is the order of increase in total exchangeable bases in those soils. When the residues were stirred up with more distilled water settling took place in the same order, there being (after 5 days) a shallow transparent zone above a thick gelatinous mass overlying the sand and coarse particles. On being allowed to dry the surface layer of fine particles exhibited shrinking to a remarkable degree.

The pH values of those coloured solutions varied from 5 to 7depending apparently upon the completeness of removal of soluble salts, and the concentrations lay between .14 and .20 per cent. The residue obtained on evaporation consisted roughly of equal parts of mineral /

mineral and organic matter. When taken up again with water it gave a solution similar to the original one. The ultramicroscope revealed the presence of ultramicrons in each liquid. The particles varied over a long range of sizes, some being almost as small as those of a gold sol, others being larger than those of a benzion sol. In every case they migrated to the anode and were therefore negatively charged.

The phenomena described support the idea that a soil complex saturated with a univalent base (hydrogen was probably also present) is very stable when soluble salts are removed. It may be readily washed out of a soil and decrease the absorptive capacity.

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